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Conformational Characteristics of Poly(vinylidene fluoride)

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ABSTRACT: Approximate conformational energy estimates have been utilized to evaluate the rotational isomeric state (RIS) model of poly(vinylidene fluoride) (PVDF). Conformational properties including the unperturbed dimensions and dipole moments and their temperature dependence and the conformational contribution to the entropy of fusion were calculated for PVDF from its RIS model. Occasional (0–20%) head to head:tail to tail (H–H:T–T) addition of monomer units in a random fashion was accounted for in the calculation of these conformational properties. In general it was found that the calculated conformational properties of PVDF were relatively insensitive to the amount of H–H:T–T addition assumed, but were instead markedly dependent upon the value of the dielectric constant (ϵ) selected to mediate the electrostatic interactions encountered along a PVDF chain. For values of $\epsilon \approx 4$–6, both the unperturbed dimensions and entropy of fusion recently measured and reported by Welch and by Nakagawa and Ishida, respectively, are reproduced by the calculations. Based on a comparison of dimensions it appears that at equilibrium PVDF adopts conformations which are on the average more compact than those assumed by either poly(ethylene) or poly(tetrafluoroethylene), the two homopolymers whose repeat units in regular alternation constitute the PVDF chain.

In recent years the effort to determine and understand the physical properties of poly(vinylidene fluoride) (PVDF) has intensified. This increased activity most probably reflects an interest in the piezoelectric and pyroelectric properties[3–12] exhibited by permanently polarized electret films of PVDF. As a result, this activity has focused primarily on the study of PVDF solid state properties.

The structures of the three crystalline forms of PVDF have been studied by x-ray diffraction[13–19] and infrared[20–25] and Raman[25] spectroscopy. Effects of specimen annealing as manifested by specific volume, differential scanning calorimetry, and electron microscopy measurements[2] have yielded the equilibrium melting point, the enthalpy and entropy of fusion, and estimates of the surface free energy, enthalpy, and length of the chain folds in PVDF crystals.

The motions of PVDF chains in the solid state have also been examined. Temperature- and frequency-dependent studies of the various relaxations observed in solid PVDF samples by dielectric,[26–37] mechanical,[33] and wide line nuclear magnetic resonance[15,30,33,38,39] (NMR) spectroscopy have been reported and associated with either the amorphous or crystalline portions of this semicrystalline polymer.

In contrast to the extensive work reported on the solid state properties of PVDF and aside from the ca. 5% head to head: tail to tail (H–H:T–T) monomer addition detected[40] in PVDF by high-resolution ^{19}F NMR spectroscopy in solution, it is only very recently that its dilute solution properties have begun to be studied. Solution viscosity and light-scattering studies by Welch[1] have led to an estimate of the unperturbed dimensions of isolated PVDF chains. It was Welch's work that prompted the present detailed study of the conformational characteristics of isolated PVDF chains described below.

Conformational energy estimates were performed on segments of PVDF chains in an attempt to determine the rotational isomeric state (RIS) model appropriate to this polymer. In addition to the predominant head to tail (H–T) arrangement of monomer units, H–H:T–T monomer addition was explicitly considered. In a departure from previous calculations,[18,41] which considered only regularly repeating structures, all rotational conformations were permitted.

Several properties characteristic of the conformational behavior of PVDF chains were calculated from its derived RIS model. The mean-square end-to-end distance and dipole moments and their temperature dependence and the conformational contribution to the entropy of fusion were calculated for isolated and unperturbed PVDF chains of high molecular weight. The calculated dimensions and entropy were compared to the appropriate experimental quantities.

Description of Calculations

Portions of a PVDF chain whose conformations depend on one or both of two neighboring backbone bond rotation angles are illustrated in Figure 1. Segments labeled HFH and FHF are characteristic of the predominant H–T addition, while the less abundant H–H:T–T arrangements are denoted as FFH(HFF) and HHF(FHH). The conformational energies of each of these fragments were calculated as a function of the rotation angles Φ_1 and Φ_2 using approximate potential functions which account for the intrinsic threefold torsional potential about the C–C backbone bonds and the van der Waals and electrostatic interactions between nonbonded atoms.

A barrier of 3.0 kcal/mol was assumed[42] to separate the three rotational minima at Φ_1 or $\Phi_2 = 0°$ (trans, t), $\pm 120°$ (gauche$^\pm$, g$^\pm$). Partial charges of +0.4 and −0.2 esu were assigned to the carbon and fluorine atoms of the CF_2 groups based on the observed C–F bond dipole moment.[18,43,44] These partial charges assigned to the carbon and fluorine atoms lie midway between the values employed by Hasegawa et al.[18] and Bates and Stockmayer.[43,44]

The value of the dielectric constant ϵ assumed to mediate the electrostatic interactions between the partially charged atoms was varied over the range $\epsilon = 2$–10, because of the un-

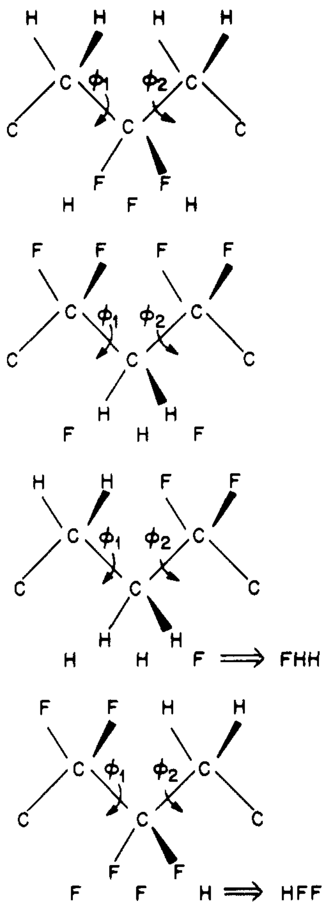

Figure 1. Chain fragments of PVDF considered in conformational energy calculations. HFH and FHF fragments correspond to H-T addition, while the HHF(FHH) and FFH(HFF) fragments represent the H-H:T-T addition of monomer units.

certainty in the value appropriate to PVDF.[18,34,41] A 6-12 potential, whose constants are taken from the work of Brant et al.[45] and Bates[43] (see Table I), was used to evaluate the nonbonded van der Waals interactions. Bond lengths of 1.53 and 1.36 Å were used for the C-C and C-F bonds, respectively, and the valence angles determined in the x-ray diffraction studies of PVDF by Hasegawa et al.[19] were assumed, i.e., ∠H-C-H = 109.5°, ∠F-C-F = 103°, ∠C-CH$_2$-C = 116.5°, and ∠C-CF$_2$-C = 118.5°. Both rotation angles Φ_1 and Φ_2 in each fragment were stepped in 20° increments over their entire ranges, and statistical weights $SW_{\alpha\beta}$ were evaluated for each of the nine pair-wise dependent rotational states $\alpha\beta$ = tt, tg$^\pm$, g$^\pm$t, g$^\pm$g$^\pm$, and g$^\pm$g$^\mp$. As an example, SW_{tg^+} was obtained from

$$SW_{tg^+} = \frac{\sum_{\Phi_1=-60^\circ}^{60^\circ} \sum_{\Phi_2=60^\circ}^{180^\circ} \exp[-E(\Phi_1,\Phi_2)/RT]}{\sum_{\Phi_1=0}^{360^\circ} \sum_{\Phi_2=0}^{360^\circ} \exp[-E(\Phi_1,\Phi_2)/RT]}$$

where the sums in both the numerator and denominator were evaluated only for those conformations (Φ_1,Φ_2) whose energies $E(\Phi_1,\Phi_2)$ are within 5.0 kcal/mol of the lowest energy conformation found.

Statistical weight matrices **U** were constructed from the statistical weights calculated at a given temperature.

$$U_{HFH} = \begin{array}{c|ccc} \Phi_1 \backslash \Phi_2 & t & g^+ & g^- \\ \hline t & SW_{tt} & SW_{tg^+} & SW_{tg^-} \\ g+ & SW_{g^+t} & SW_{g^+g^+} & SW_{g^+g^-} \\ g- & SW_{g^-t} & SW_{g^-g^+} & SW_{g^-g^-} \end{array}$$

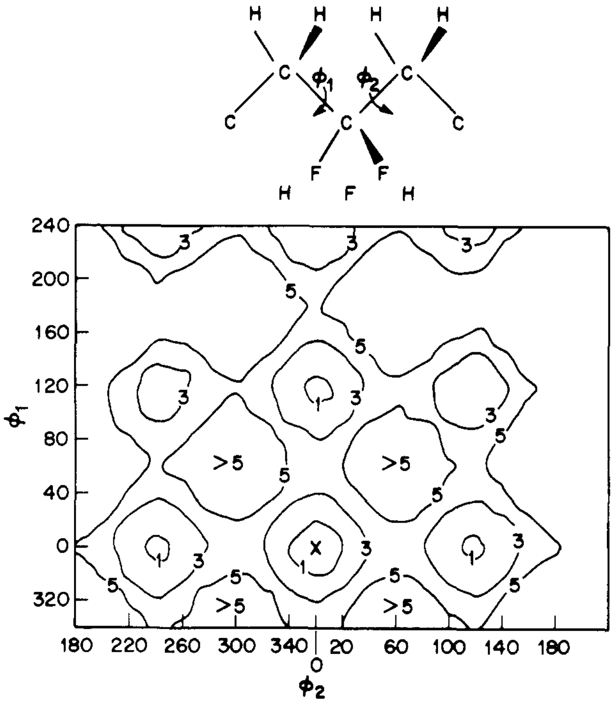

Figure 2. Conformational energy map calculated at ϵ = 6 for the HFH fragment of PVDF. Energy contours are given in kcal/mol of HFH fragment relative to the lowest energy conformation located at X.

Table I
6-12 Potential Constants A_{ij} and C_{ij} Used to Evaluate the Nonbonded van der Waals Interactions
($A_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^{6}$)

Atom pair, ij	C_{ij}, (kcal Å^6)/mol	A_{ij}, (kcal Å^{12})/mol
H-H	46.5	7 180
C-C	361	393 130
F-F	118	43 000
H-C	126	56 000
H-F	63.7	15 350
C-F	196	126 200

These statistical weight matrices were then used in conjunction with matrix multiplication methods[46] to calculate mean-square end-to-end distances $\langle r^2 \rangle_0$ and dipole moments $\langle \mu^2 \rangle_0$ and the conformational entropy[47] S_a of isolated unperturbed PVDF chains. PVDF chains with from 0 to 20% of the monomer units added randomly in a H-H:T-T fashion were generated by Monte Carlo techniques and used to calculate the effect of H-H:T-T addition on the isolated chain properties $\langle r^2 \rangle_0$, $\langle \mu^2 \rangle_0$, and S_a. Ten Monte Carlo chains were generated at each H-H:T-T defect content.

Calculated Results. A conformational energy map calculated at ϵ = 6 for the HFH chain fragment in PVDF is presented in Figure 2. The tt (Φ_1 = Φ_2 = 0°) conformation is favored for all ϵ, but at higher (lower) ϵ the stabilities of the other rotational states are increased (decreased) relative to the tt state. For the FHF fragment the g$^\pm$g$^\pm$, tg$^\pm$, and g$^\pm$t states are most stable, and as ϵ is increased the tt and g$^\pm$g$^\mp$ states begin to contribute significantly to the ensemble of conformations. Consequently, as ϵ increases, thereby reducing the electrostatic interactions, both the calculated dimensions and dipole moments are reduced and the conformational entropy increased as the number and probabilities of compact conformations permitted increase (see below).

The calculated dimensions and dipole moments of long

Table II
Calculated Dimensions and Dipole Moments of PVDF

	CR = $\langle r^2\rangle_0/nl^2$ T, °C				CM = $\langle \mu^2\rangle_0/nm^2$ T, °C		
ϵ	25	85	190	210	25	85	210
2		14.5–10.7[a]	11.8–9.54[a]	11.3–9.32[a]			
4		7.54[b]	6.43[b]	6.22[b]			
6	6.40[c]	5.76[c]	5.06[c]	4.93[c]	1.11–0.84[a]	1.03–0.80[a]	0.92–0.76[a]
10		4.30[c]	3.94[c]	3.87[c]			

[a] Range corresponds to 0 to 20% H–H:T–T addition. [b] 0% H–H:T–T addition. [c] Insensitive to % H–H:T–T addition.

Table III
Temperature Coefficients of the Calculated Dimensions and Dipole Moments of PVDF

ϵ	d ln $\langle r^2\rangle_0$[a]/dT × 10^3	d ln $\langle \mu^2\rangle_0$[a]/dT × 10^3
2	−1.96 to −1.12[b]	
4	−1.54[c]	
6	−1.26[d] (−1.75)[e]	−1.00 to −0.49[b]
10	−0.84[d]	

[a] Calculated over the temperature interval T = 85–210 °C. [b] Range corresponds to 0 to 20% H–H:T–T addition. [c] 0% H–H:T–T addition. [d] Insensitive to % of H–H:T–T addition. [e] Calculated over the temperature interval T = 25–85 °C.

Table IV
Conformational Entropies Calculated for 500 Bond PVDF Chains at the Melting Point T = 210 °C

	S_a, eu/bond				
ϵ	0[a]	5	10	15	20
2	1.54	1.54	1.53	1.52	1.52
4	1.94				
6	2.05	2.05	2.05	2.04	2.04
10	2.13				

[a] % H–H:T–T addition.

PVDF chains (500 bonds) with from 0 to 20% of the monomer units added randomly H–H:T–T are presented in Table II at several temperatures and for ϵ = 2, 4, 6, 10. Both the dimensions and dipole moments are expressed as ratios CR and CM, respectively, where CR = $\langle r^2\rangle_0/nl^2$, CM = $\langle \mu^2\rangle_0/nm^2$, and n is the number of bonds, l^2 is the C–C bond length squared, and m^2 is the square of the net CF_2 dipole moment along the CF_2–CH_2 backbone bond. Table III contains the temperature coefficients of both the dimensions and the dipole moments. Conformational entropies calculated at the melting point (210 °C)[2] as a function of ϵ and the amount of H–H:T–T addition are listed in Table IV.

Discussion of Results

It is clear upon examination of the results presented in Tables II–IV that the conformational properties calculated for PVDF are much more sensitive to the value of ϵ employed than to the degree of H–H:T–T addition assumed. When it is remembered that typically[40] only 5% of the monomer units in PVDF are added in a H–H:T–T fashion, then it seems reasonable to ignore the effects of this small percentage of reversed monomer units on the conformational properties of isolated PVDF chains in solution or in the disordered melt.

Welch[1] has found that benzophenone at 190 °C is a theta solvent for PVDF by employing a combination of viscosity and light-scattering measurements. From the intrinsic viscosity–molecular weight relation observed in benzophenone at 190 °C, Welch was able to determine[48] the unperturbed dimensions of PVDF which led to CR = 5.6 ± 0.3. This value can be reproduced by the calculated dimensions (see Table II) if $4 < \epsilon < 6$.

This value of ϵ is smaller than the solvent dielectric constant (ϵ = 11.4 at 50 °C for benzophenone),[50] but probably exceeds that of the isolated polymer chain, since ϵ = 2.2 for amorphous poly(ethylene) (PE)[51] and 2.0 for amorphous poly(tetrafluroethylene) (PTFE),[51] the two homopolymers whose repeat units in alternation constitute the PVDF chain. A value of ϵ = 4–6 is therefore not unreasonable for PVDF dissolved in a polar solvent like benzophenone.

The following statistical weight matrices are appropriate for PVDF at ϵ = 6 and T = 190 °C: for H–T addition

$$U_{HFH} = \begin{bmatrix} 1.0 & 0.559 & 0.559 \\ 0.559 & 0.255 & 0.124 \\ 0.559 & 0.124 & 0.255 \end{bmatrix}$$

$$U_{FHF} = \begin{bmatrix} 0.607 & 0.848 & 0.848 \\ 0.848 & 1.0 & 0.770 \\ 0.848 & 0.770 & 1.0 \end{bmatrix}$$

and for H–H:T–T addition

$$U_{HHF} = \begin{bmatrix} 0.927 & 0.920 & 0.920 \\ 1.0 & 0.830 & 0.517 \\ 1.0 & 0.517 & 0.830 \end{bmatrix}$$

$$U_{FFH} = \begin{bmatrix} 1.0 & 0.787 & 0.787 \\ 0.653 & 0.446 & 0.310 \\ 0.653 & 0.310 & 0.446 \end{bmatrix}$$

$$U_{FHH}(I,J) = U_{HHF}(J,I)$$

$$U_{HFF}(I,J) = U_{FFH}(J,I)$$

The unperturbed dimensions of PVDF are smaller than those of PE and PTFE,[46] and on this basis it appears that at equilibrium PVDF adopts conformations which are on the average more compact than those assumed by either of the two homopolymers (PE and PTFE) whose repeat units in regular alternation constitute the PVDF chain.

From the conformational energies and entropies calculated here for unperturbed PVDF chains, it is possible to estimate the contribution to the total entropy of fusion made by the increase in conformational freedom of PVDF chains upon melting. This contribution ΔS_{conf} is simply the difference between the conformational entropies of molten amorphous and crystalline PVDF chains $S_a - S_c$.

Table V
Calculated Conformational Entropies[a] of Amorphous and Crystalline PVDF Chains of 500 Bonds

% H–H:T–T	Crystalline form	$\epsilon = 2$			$\epsilon = 4$			$\epsilon = 6$			$\epsilon = 10$		
		S_a	S_c	ΔS_{conf}	S_a	S_c	ΔS_{conf}	S_a	S_c	ΔS_{conf}	S_a	S_c	ΔS_{conf}
0	I	1.54	0.81	0.73	1.94	0.58	1.36	2.05	0.48	1.57	2.13	0.39	1.74
0	II	1.54	1.84	−0.30	1.94	1.11	0.83	2.05	0.70	1.35	2.13	0.48	1.65
5	I	1.54	0.75	0.79				2.05	0.48	1.57			
5	II	1.54	1.80	−0.26				2.05	0.66	1.39			
10	I	1.53	0.65	0.88				2.05	0.46	1.59			
10	II	1.53	1.74	−0.21				2.05	0.63	1.42			
15	I	1.52	0.57	0.95				2.04	0.45	1.59			
15	II	1.52	1.69	−0.17				2.04	0.58	1.46			
20	I	1.52	0.50	1.02				2.04	0.44	1.60			
20	II	1.52	1.64	−0.12				2.04	0.54	1.50			

[a] All entropies are expressed in eu/mol of bonds.

Amorphous chain entropies are given in Table IV, and the conformational entropy of crystalline PVDF chains S_c can be obtained by dividing the intramolecular conformational energy of the crystalline conformation by the melting temperature. The two dominant crystalline forms of PVDF, forms I and II, are characterized[18,19] by all trans planar zigzag and alternating tg^+ and tg^- conformations about the bonds flanking the CH_2 groups, respectively. In Table V are presented the entropies S_a, S_c, and $\Delta S_{conf} = S_a - S_c$ calculated for PVDF chains with varying H–H:T–T contents, different crystalline forms, and using a range of dielectric constants.

It has been shown[47] that the fusion of crystalline polymers can be separated into two independent contributions. An intramolecular contribution $(\Delta S_\mu)_V$ occurring at constant volume and an intermolecular contribution ΔS_V due to volume expansion sum to yield the total entropy of fusion $\Delta S_\mu = (\Delta S_\mu)_V + \Delta S_V$. In addition the constant volume or intramolecular contribution to the entropy of fusion has been shown[47] to be closely approximated by the change in conformational entropy accompanying the melting process in a wide variety of synthetic crystalline polymers, i.e., $(\Delta S_\mu)_V \approx \Delta S_{conf}$ and $\Delta S_{conf} < \Delta S_\mu$.

Nakagawa and Ishida[2] have measured the entropy of fusion of form II PVDF with ca. 5% of the monomer units added in H–H:T–T fashion and found $\Delta S_\mu = 1.65$ eu/mol of bonds. Clearly, then, $\Delta S_{conf} < 1.65$ eu/mol of bonds for PVDF. The calculated changes in the conformational entropy of PVDF upon melting presented in Table V are insensitive to the degree of H–H:T–T addition but rule out values of $\epsilon \leq 2$ and $\epsilon \geq 10$, because ΔS_{conf} is either negative or larger than ΔS_μ for these values. Dielectric constants in the range $2 < \epsilon < 10$ lead to values of ΔS_{conf} which are consistent with the measured entropy of fusion. It is worth noting that this range of dielectric constants encompasses the range $4 < \epsilon < 6$ found necessary to produce calculated dimensions in agreement with experiment.

It is of interest to compare the dimensions of PVDF with those of poly(isobutylene) (PIB) and poly(vinylidene chloride) (PVDC), the only other polymers of the structural type $(\text{-}CH_2\text{-}CR_2\text{-})_x$ whose unperturbed dimensions have been measured.[46,52] At 25 °C CR = 6.6 and 8.1 for PIB and PVDC, respectively. Extrapolation and enterpolation of the dimensions calculated for PVDF with $4 \leq \epsilon \leq 6$, which reproduce the measured dimensions at 190 °C, leads to CR = 7.4 at 25 °C (see Tables II and III). Thus, as manifested by unperturbed dimensions PVDF seems to be midway between PIB and PVDC with regard to its equilibrium chain flexibility.

The apparent ordering of dimensions PVDC > PVDF > PIB may be rationalized if the differences in van der Waals radii and polarity between the CH_3, Cl, and F substituents is considered. As discussed by Matsuo and Stockmayer,[52] the electrostatic repulsion between Cl atoms more than compensates the reduction in size of a Cl atom relative to a CH_3 group and leads to the stabilization of helical g^+g^+ and g^-g^- sequences at the expense of the tt sequence resulting in larger dimensions for PVDC compared to PIB. Since the electrostatic interactions in PVDF and PVDC are nearly identical and because the F atom is smaller than the Cl atom, stabilization of the g^+g^+ and g^-g^- helical sequences in PVDF is not as pronounced as in PVDC resulting in dimensions intermediate between PIB and PVDC.

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Conformational Transitions of Polypeptides in Ternary Solvent Systems

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ABSTRACT: Phase diagrams for conformational transitions of polypeptides in ternary organic solvent systems containing two active and one inert component are calculated for a model which takes into account possible interaction of the two active components with each other as well as with the polypeptide backbone. The results of experimental determinations of conformational transitions and isothermal phase boundaries for poly(β-benzyl L-aspartate) (PBA) in three-model solvent systems are in generally good accord with the theory. The solvent systems are: (a) 1-chloropropionic acid–dichloroacetic acid (DCA)–1,1,2,2-tetrachloroethane (TCE), (b) monochloroacetic acid–DCA–TCE, and (c) dimethyl sulfoxide–DCA–TCE.

Conformational transitions in organic solvent soluble polypeptides are commonly studied in binary solvent mixtures in which the solute–solvent interaction of one component is indifferent to the conformational state of the polymer, while the second component is to some extent capable of competitively hydrogen bonding with the peptide and thereby disrupting the helix or other ordered conformation. These solvent constituents are commonly referred to as the inert and active components, respectively. A few studies have been carried out in which both components are nominally in the active class;[1] in this case a more complicated description involving multiple competitive equilibria between the solute and the two active components and between the two solvents themselves would be necessary. The possible interaction of adjacent filled bonding sites on the macromolecule could also be taken account in a complete treatment and the presence of a third, inert, solvent which serves to modify the activities of the helix-disrupting constituents should be allowed for.

We wish to report here a theoretical treatment of conformational transitions of polypeptides in such ternary mixed solvents, together with the results of relevant experimental studies in which the isothermal helix–coil transition of poly(β-benzyl L-aspartate) (PBA) has been investigated in three different solvent systems. For each example we have chosen a strong and moderately weak active solvent together with an appropriate inert solvent. The latter was 1,1,2,2-tetrachloroethane (TCE), and the strongly helix disrupting solvent was dichloroacetic acid (DCA) throughout, while the weaker bonding solvents were (a) monochloroacetic acid (MCA), (b) 1-chloropropionic acid (CPA), and (c) dimethyl sulfoxide (DMSO), respectively.

Isothermal conformational phase equilibria involving ternary solvent systems can be most appropriately represented using an equilateral triangle, in which the apices represent the pure components, and the sides the mole fractional compositions of the respective binary solvent pairs. Any interior point is then simply related to the mole fractional composition of the ternary solvent mixture. The triangle itself constitutes an isothermal section of a right angular equilateral prism whose vertical coordinate represents temperature. We are considering here the phase boundary (or boundaries) separating domains containing helical and random-coil conformations, where the phase boundary is defined, as usual, as the locus of the points at which the average fractional helical content of the polypeptide is 0.5.

Theory

The equilibrium constant, s, describing the helix–coil equilibrium in the presence of a mole fraction x_A of an active solvent A in an active–inert (I) solvent mixture is given by[2]

$$s = K_1K_{2A}/(K_{2A} + x_A) \qquad (1)$$

where K_1 and K_{2A} are the equilibrium constants, at a given temperature, relating to intramolecular (peptide–peptide) and intermolecular (peptide–solvent) interactions, respectively. In the presence of a mole fraction x_B of a second active solvent, B, eq 1 is modified:

$$s = \frac{K_1K_{2A}K_{2B}}{K_{2A}K_{2B} + x_A'K_{2B} + x_B'K_{2A}} \qquad (2)$$

the constants K_{2A} and K_{2B} now referring to the individual interactions of A and B with the polypeptide. The quantities x_A' and x_B' are the effective mole fractions of free A and B available for this interaction, taking into account the possible formation of a mole fraction x_{AB}' of the complex AB. The