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A SEMI-EMPIRICAL METHOD FOR PREDICTION OF CRITICAL CONCENTRATIONS FOR POLYMER OVERLAP IN SOLUTION

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Abstract—The hydrodynamic volumes of solvated polymers shrink with increasing concentrations in solution until a concentration (c_x) is reached at which the effective dimensions are the same as those in a Flory theta solvent. Further increases beyond c_x result in progressively greater overlapping of separate macromolecules. Several theories are available for the prediction of c_x but none is entirely satisfactory. A semi-empirical method is described here for the estimation of c_x, using intrinsic viscosities as input parameters. The magnitude of c_x is shown to be solvent dependent; its lower limit is zero, in a theta solvent.

INTRODUCTION

A relation developed in this laboratory between the dimensions and concentrations of solvated polymers has proved to be a useful tool for predicting a variety of solution properties of macromolecules. It has provided correct estimations of polymer dimensions in solution [1], accounted for concentration efforts in GPC [2, 3] and has been applied in the rationalization of the effects of shear stresses on the degradation of polymers [4, 5]. The model has also been extended to predict osmotic pressures [6], second virial coefficients [7] and Flory–Huggins interaction parameters [8].

This article is mainly concerned with the critical concentration, c_x which is a parameter in this theory. Solvated polymers decrease in size with increasing concentration and a critical concentration, c_x is defined in our model [1] as that concentration at which the macromolecular coils reach their unperturbed dimensions. No further shrinkage occurs at concentrations greater than c_x although the macromolecules become progressively more overlapped in this region. The theory used to date calculates a value for c_x which is independent of solvent quality. In a previous article [3], we have pointed out that this is unsatisfactory, since c_x should be zero for a theta solvent (where macromolecules at any concentration are at their unperturbed dimensions) and should increase as the solvent becomes progressively better.

A method for overcoming this deficiency is reported here. We have made use of intrinsic viscosities as input parameters, as in previous applications of this model [1–3, 6–8]. The procedure outlined here is semi-empirical but it provides good accordance with all the relevant published experimental data which we could find.

THEORY

According to the Rudin model [1], the hydrodynamic volume, $v\epsilon$, of a polymer molecule in solution is given by:

$$v\epsilon = \frac{4\pi[\eta]M\phi_x}{9.3 \times 10^{24}\phi_x + 4\pi N_0 c([\eta] - [\eta]_\theta)} \qquad (1)$$

and the critical concentration c_x at which polymer molecules are at their theta condition is:

$$c_x = \frac{9.3 \times 10^{24}\phi_x}{4\pi N_0[\eta]_\theta}. \qquad (2)$$

In the above equation v is the unperturbed volume (cm^3) of a polymer molecule with molecular weight M and ϵ is a dimensionless swelling factor which is equivalent to α_η^3 in Flory's notation [9]. Also, $[\eta]$ is the intrinsic viscosity (cm^3 g^{-1}) of the polymer in the solvent of interest while $[\eta]_\theta$ is its intrinsic viscosity in a theta solvent. The polymer concentration is c (g cm^{-3}), N_0 is Avogadro's constant and ϕ_x is the volume fraction of solvated polymer at which the polymer coils have shrunk to their unperturbed dimensions (i.e. $\epsilon = 1$). Originally Rudin and Wagner [1] assigned a value of unity to ϕ_x. The magnitude of $v\epsilon$ is not very sensitive to the choice of ϕ_x since this parameter occurs in both the numerator and denominator in Eqn (1) and the first term in the denominator in the right-hand side term$\gg$ the second term. The magnitude of c_x is strongly affected, however, as can be seen in Eqn (2). As mentioned, ϕ_x should vary with solvent quality, being zero for a theta solvent and increasing as the solvent becomes progressively better. We will assume here that $\phi_x = 1$ in the case of a hypothetical "ideal" solvent. Further, it is assumed that ϕ_x is a linear function of the difference $[\eta] - [\eta]_\theta$. Intrinsic viscosities are useful parameters to use in this context because $[\eta]$ is easily measured

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[10] and $[\eta]_\theta$ can be estimated readily [11]. Their use here is also consistent with the cited earlier applications of this model. The assumptions and boundary conditions described lead to:

$$\phi_x = \frac{[\eta] - [\eta]_\theta}{[\eta]_I - [\eta]_\theta}, \qquad (3)$$

where $[\eta]_I$ refers to the intrinsic viscosity of the polymer with molecular weight M in the hypothetical ideal solvent. ϕ_x ranges between 0 and 1 under theta and ideal solvent conditions, respectively.

The intrinsic viscosity of monodisperse polymer with molecular weight M is given by the Mark–Houwink equation:

$$[\eta] = KM^a, \qquad (4)$$

where K and a are the appropriate constants. For flexible chains, a has been shown to range from 0.5 for a theta solvent to 0.8 for the limiting case of a very good solvent [12]. The final expression needed for ϕ_x is then:

$$\phi_x = \frac{KM^a - K_\theta M^{0.5}}{K_I M^{0.8} - K_\theta M^{0.5}}. \qquad (5)$$

Here K_I and K_θ are the Mark–Houwink pre-exponential constants for ideal and theta solutions, respectively.

Van Krevelen and Hoftyzer [13] have shown that K, K_θ and a are correlated by the relationship

$$-\log(K/K_\theta) = 3.7 \pm 0.7(a - 1/2). \qquad (6)$$

Hence, K_I can be obtained if the limiting value of $a = 0.8$ and the appropriate K_θ are inserted into the above equation:

$$-\log(K_I/K_\theta) = 3.7(0.8 - 0.5) = 1.11. \qquad (6a)$$

An alternative procedure uses the experimental value of K at which $a = 0.8$ for the polymer is question; this method is, of course, applicable only when a value of 0.8 has been obtained experimentally.

RESULTS

The results obtained using Eqns (2), (5) and (6a) are shown in column 6 of Table 1, together with experimental results cited in the literature. For those cases in which experimental K_I are available, the c_x values obtained are shown in column 7. Generally, there is not much difference between results of columns 6 and 7. The agreement with experimental results is good.

The Mark–Howink constants for the polystyrene–carbon disulphide system in Table 1 were not available in the literature. We have estimated $\phi_x \simeq 0.9$, since carbon disulphide was reported [20] to be a very good solvent for polystyrene.

The Mark–Houwink constants, K and a, used in calculations with Eqn (5) are given in Table 2. The K_θ and K_I values for the various polymers examined are listed in Table 3.

DISCUSSION

The method suggested here for the estimation of critical concentrations appear to give good agreement with experimental results. A simple relationship between ϕ_x and $[\eta]$ seems to have accounted well for the variation of the size of the solvated polymer coil with solvent quality and molecular weight of the macromolecule. In the context of the Rudin model, the calculated value of c_x represents the concentration at which polymer coils have shrunk to their unperturbed dimensions.

According to scaling law concepts, there exist two critical concentrations c_s^* and c_s^{**} [21, 22]; c_s^* represents the onset of overlapping of polymer chains, while c_s^{**} marks the end of the transition from the dilute to the semi-dilute regime. In the above comparison with experimental results, we have identified c_s^* with our c_x.

A method of estimating c_s^* is due to Simha and coworkers [33, 34], in which

$$c_s^* = \frac{1}{[\eta]}. \qquad (6)$$

Figure 1 compares c_s^* calculated from Eqn (6), together with those from column 6 of Table 1. (A comparison with column 7 gives the same conclusion.) We have only compared calculated values with experimental up to $c_x = 2.5 \times 10^{-2}$ g ml^{-1}. Higher c_x values correspond to molecular range of less than 200,000. The transition of the physical properties measured with concentration for this range of molecular weight is usually not sharp. A quantitative comparison between experimental and predicted results in this lower molecular weight range may thus be unrealistic. The method suggested here seems to give better overall agreement with experimental results as judged by the dispersion of the points about the line indicated for c_x (predicted) vs c_x (expt.).

For theta solvents, the present method predicts zero critical concentrations. This conclusion is supported by the X-ray scattering results of Hayashi *et al.* [35] and also by light scattering results of Benoit and Picot [17]. On the other hand, Aharoni [16] reported critical concentrations for polystyrene in decalin (a poor solvent) and cyclohexane (a theta solvent) equal to that in benzene. This discrepancy must await further experimental investigation before it can be resolved.

In the above comparison with experimental data, we have left out the classical method of viscometry [36]. This method generally gives much higher values of critical concentrations. This has been attributed to the fact that the method is not sensitive enough to detect the initial onset of overlapping of polymer chains [16].

We recommend the use of K_θ cited in the literature rather than calculated values. We have tried the use of the modified form of the Fox–Flory equation [37, 38]

$$K_\theta = \frac{0.21\beta^3}{M_0^{3/2}}, \qquad (7)$$

in which $\beta \approx$ three times the carbon-carbon bond distance (in Å) and M_0 is half the formula weight of the repeating unit. K_θ obtained for polystyrene is much lower than the experimental value. The difficulty is in estimating β. K_θ is very sensitive to the value of β. The alternative value of 0.25 for the coefficient in the above equation only gives slight improvement.

Table 1. Comparison of experimental and predicted critical concentrations

	Polymer	Solvent	Mol wt	Method	$c_x \times 10^2$ (g ml^{-1})			Ref.
					Expt	From Eqns (2), (5) and (6a)	From Eqns (2), (5) and K_l from literature	
1.	Poly(styrene) PS	Tetrahydrofuran	1.8×10^6	Gel-permeation chromatography	0.9	0.6	0.9	3
2.	PS*	Toluene	1.1×10^5	X-ray scattering	5.0	2.4	4.1	14
3.	PS	Benzene	1.3×10^6	Light scattering	0.55	0.66	0.96	15
			2.4×10^6		0.53	0.47	0.67	
			3.8×10^6		0.40	0.36	0.51	
			7.1×10^6		0.35	0.26	0.36	
4.	PS	Benzene	2.05×10^6	Light scattering	0.5	0.5	0.7	16
			2.0×10^5		2.5	1.8	2.9	
5.	PS	Tetrahydrofuran	2.05×10^6	Light scattering	0.5	0.6	0.8	16
			2.0×10^5		2.5	1.7	2.8	
6.	PS*	Benzene	7.5×10^6	Light scattering	0.2	0.25	0.35	17
		Methylethyl ketone (MEK)	7.8×10^6		0.1	0.1	0.1	
7.	Poly(methyl methacrylate)*	MEK	1.8×10^6	Light scattering	0.4	0.6	0.5	17
8.	PS	Toluene	1.5×10^4	Osmotic pressure	>8.0	7.6	11.9†	18
9.	PS	Toluene	3.1×10^5	Osmotic pressure	1.3	1.3	2.0	19
10.	PS*	Carbon disulphide	1.07×10^5	Neutron scattering	5.1‡	4.0	4.0	20
11.	PS	Tetrahydrofuran	1.8×10^5	Quasi-elastic light scattering	3.26§	1.8	2.9	21
			3.9×10^5		1.93	1.27	1.96	
			3.0×10^6		0.48	0.47	0.67	
			1.0×10^7		0.21	0.25	0.36	
12.	PS	1,2-Dichloroethane	1.11×10^5	Excimer fluorescence	3.05	1.68	2.90	22
			3.92×10^5		1.20	0.82	1.25	
			9.0×10^5		0.58	0.50	0.74	
13.	Poly(vinyl pyrrolidone)	Water	5.6×10^5	Diffusion	0.47	0.51	—	23
			5.0×10^4		2.07	2.86	—	

* Results interpolated from plots given in references cited.

† $[\eta]_l$ taken to be equal to $[\eta]$ since in the computation $[\eta]$ is slightly greater than $[\eta]_l$.

‡ Density of CS_2 is 1.2632 g ml^{-1}. The value interpolated from Ref. [20] = 4.0% (wt/wt).

§ Calculated according to Eqn (6) of Ref. [21].

Table 2. Mark–Houwink constants used in calculations

		Temp.	$K \times 10^3$ (ml g^{-1})	a	Ref
Polystyrene	Tetrahydrofuran	25	6.82	0.766	24
	Toluene	25	17.0	0.69	25
	Benzene	20	12.3	0.72	26
	Methyl ethyl ketone	25	39.0	0.58	25
	1,2-Dichloroethane	25	21.0	0.66	25
Poly(methyl methacrylate)	Methyl ethyl ketone	25	9.39	0.68	27
Poly(vinyl pyrrolidone)	Water	30	39.3	0.59	28

Table 3. K_θ and K_l values used in calculations

	$K_\theta \times 10^3$ (ml g^{-1})	Ref	$K_l \times 10^3$ (ml g^{-1}) (from Eqn [6a])	$K_l \times 10^3$ (ml g^{-1}) (from literature)	Ref
Polystyrene	84.6	25	6.57	4.9*	29
Poly(methyl methacrylate)	48.0	30	3.73	4.85	31
Poly(vinyl pyrrolidone)	75.0	32	5.82	—	

* $a = 0.79$ (nearest figure available).

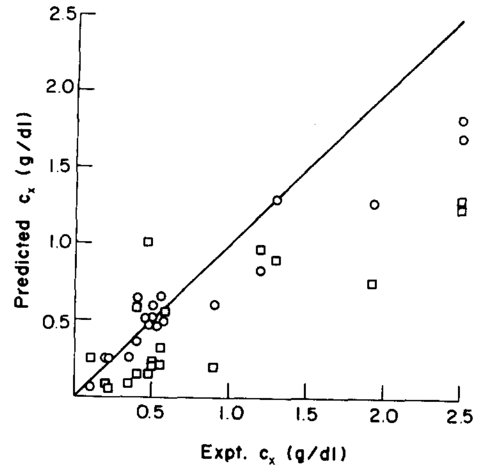

Fig. 1. Comparison of methods for estimating c_x: ○ from Eqns (2), (5) and (6a); □ from Eqn (6).

Although the present method is artificial to a certain extent, it provides a feasible way to calculate c_x for flexible polymer chains. K_l can be estimated from Eqn (6a) or, preferably, obtained from the literature. Either method should give good estimations for molecular weights greater than 200,000. It is hoped that, as more experimental data are made available, the model can be further tested and improved for other polymer systems.

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