Polymer 49 (2008) 4740–4744

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Transition of hydration states of poly(vinyl alcohol) in aqueous solution

Wenbo Li [a], Yun Zheng [a], Rongshi Cheng [a,b,*]

[a] Key Laboratory for Mesoscopic Chemistry of the Ministry of Education, Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, PR China
[b] College of Material Science & Engineering, South China University of Technology, Guangzhou, 510640, PR China

ARTICLE INFO

Article history:
Received 12 May 2008
Received in revised form 14 July 2008
Accepted 5 August 2008
Available online 20 August 2008

Keywords:
Hydration states
Poly(vinyl alcohol)
DSC

ABSTRACT

A straightforward method for determination of the hydration number of polymer in aqueous solution based on ice-melting technique of DSC is proposed. The simple yet precise method has been applied to determine the hydration number of poly(vinyl alcohol) (PVA) in aqueous solution covering a wide range of concentrations, from 0.005 to 0.3 g(solute)/g(solution), for three samples with different molar masses. The hydration number of PVA maintains a constant lower value of 2.5 when the concentration exceeds 0.2 g(solute)/g(solution). It increases to a value of 7 when the concentration decreases to the overlap concentration C^* of the polymer, where C^* was estimated as the reciprocal of its intrinsic viscosity. For solutions of $C < C^*$, the hydration number keeps constant again at the value of 7. This behavior evidently demonstrates that PVA has two hydration states, one occurs at the dilute regime and the other occurs at concentrated regime. The concentration dependent transition from one state to another is treated mathematically by a quantitative formula which involves two parameters: one denotes the transition concentration and the other denotes the width of the transition region. The transition concentration decreases linearly with increasing molar mass resembling the behavior of molar mass dependence of overlap concentration. The structural features for the two states of hydrated PVA are briefly discussed.

1. Introduction

The effect of solvation on the physical properties of polymer solution is an interesting and basic topic in polymer physical chemistry, both in theoretical and experimental aspects. It has been demonstrated that solvated solvent molecules firmly attach to polymer chains, and cannot be separated during size exclusion chromatographic separation process [1]. In other words, a "naked" polymer chain truly does not exist in the solution, and all of the polymer solution properties are due to the "dressed" polymer chains with a solvated solvent shell. Hence quantitative determination of the solvation number of each repeating unit of the polymer becomes a key problem.

There are several experimental methods to detect the change of the solvation states, especially in mixed solvents where the preferential adsorption coefficient is the most important parameter and could be deduced. Cheng et al. [1–4] developed a special technique to study this problem from the variation of the response constant of the differential refractive index detector before and after the separation in size exclusion chromatography. Recently, the states of water absorbed by water-soluble polymers including hydrogels have been widely investigated using various techniques, especially the Differential Scanning Calorimetry (DSC) method [5–15]. It is generally accepted that the states of water in water-containing hydrophilic polymer should be divided into at least two main categories, i.e., non-freezable and freezable water. The fact that the relative contents of water in different states could be differentiated and determined by DSC measurements provides an excellent tool to analyze the hydration problem quantitatively. For example, the states of water in partially swollen chemically cross-linked poly(vinyl alcohol) hydrogels and their hydration numbers were determined and analyzed by DSC ice-melting technique [15].

A solution of flexible polymer usually can be divided into three regimes, namely dilute, semi-dilute and concentrated solutions. The boundary concentration between dilute and semi-dilute solution is the overlap concentration C^*, at which individual polymer coil starts to contact with surrounding coils as proposed by de Gennes et al. [16,17]. However, accurate determination of overlap concentration is a troublesome task, since most properties of a polymer solution only change the slopes of its concentration dependency gradually at the boundary region. Liu et al. [18] in a study on physical frozen-gel formation of aqueous poly(vinyl alcohol) solutions covering a wide concentration range had simultaneously measured the fraction of polymer in solution being converted into gel (G) and the swelling ratio (Q) of the formed gel.

---

[*] Corresponding author. Key Laboratory for Mesoscopic Chemistry of the Ministry of Education, Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, PR China.
E-mail address: rscheng@nju.edu.cn (R. Cheng).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.08.029

They found that in the region where both sol and gel coexist, G increases while Q decreases with increasing concentration and the product $G \cdot Q$ shows a cusp at C^* as estimated by the reciprocal of its intrinsic viscosity. The product $G \cdot Q$ means the weight of swollen gel produced from unit weight of the initial polymer in the solution. This fact suggests that the hydration state of PVA in aqueous solution changes suddenly at C^*. In the present article, the developed principle for determining the hydration number of hydrogels is extended to water-soluble poly(vinyl alcohol). Combining two sets of data for hydrogels and solutions, a more realistic understanding of hydration process of poly(vinyl alcohol) was attained.

2. Experimental

The three poly(vinyl alcohol) (PVA) samples used in the present work are all commercial products. Their Degrees of Saponification (DS) are more than 97.0 mol% as quoted by the manufacturers. The intrinsic viscosities of these PVA samples in aqueous solution were determined at 30 °C for estimating the overlap concentration. The molecular weights of the PVA samples are calculated according to the Mark–Houwink relationship [18] as listed in Table 1.

$$[\eta] = 45.3 \times 10^{-3} M^{0.64} \tag{1}$$

The sample solutions with concentration beyond 5×10^{-2} g/g were directly prepared by dissolving known amount of dried solid PVA in de-ionized water under reflux for 2 h at a temperature of 90 °C. While the sample solutions with concentration less than 5×10^{-2} g/g were prepared by diluting a stock solution with concentration around 5×10^{-2} g/g. The exact concentrations of solutions were determined by weighing the remaining polymer after complete evaporation of water.

A TA MDSC2910 Differential Scanning Calorimeter (DSC) was used to measure the ice-melting enthalpies of PVA solutions with various concentrations. About 5–10 mg of each polymer solution with known concentrations were injected into and sealed in an aluminum pan. Empty pans were pretreated in boiling water for 1 h and then dried before use. The sealed sample pan was placed in the TA instrument and cooled to −40 °C to freeze the solution and then heated from −40 °C to 40 °C at a heating rate of 5 °C/min for avoiding the time lag of response caused by a faster heating rate. Temperatures and enthalpies of melting of the samples were calibrated using pure water as the standard. Their standard deviations were found to be within ±0.3 °C and ±0.5%, respectively.

The unit of enthalpy calculated by the DSC is usually in terms of J/g weight of solution sealed in the pan. For studying the ice-melting phenomena of an aqueous solution with a concentration of C in g(solute)/g(solution), the weight of water in the pan is $w(1-C)$ in grams, where w denotes the weight of the solution. For comparing the thermal behavior of solvent alone in a series of solutions with different concentrations, a correction should be applied to the enthalpies by dividing a term of $(1-C)$. So the fraction of the freezable free solvents in the total amount of solvent presented in solution can be expressed as:

$$F_{\text{freezable}} = \frac{\Delta H_{\text{m}}}{\Delta H_{\text{m}}^{0}(1-C)} \tag{2}$$

Table 1
The intrinsic viscosity, molecular weight and parameters for transition of hydration states of PVA samples

	$[\eta]$/(mL/g)	$M \times 10^{-5}$	d	k	C_t
PVA I	79.1	1.16	1.63	8.5	0.118
PVA II	105.4	1.82	1.82	14	0.071
PVA III	124.1	2.35	1.80	30	0.033

where ΔH_{m}^{0} is the melting enthalpy of pure water, $\Delta H_{\text{m}}^{0} = 333.5$ J/g, ΔH_{m} is the melting enthalpy of aqueous solution with concentration C in g(solute)/g(solution) experimentally determined by DSC.

Naturally, the fraction of the non-freezable solvated solvents in the presented total amount of solvent in solution is:

$$F_{\text{solvated}} = 1 - \frac{\Delta H_{\text{m}}}{\Delta H_{\text{m}}^{0} \cdot (1-C)} \tag{3}$$

The non-freezable solvated solvent molecules are firmly associated with polymer backbone and may be regarded as a portion of the solvated polymer. Then the concentration of the solvated polymer should be increased to:

$$C_{\text{solvated}} = \frac{M_0 + n \cdot M_{H_2O}}{M_0} \tag{4}$$

Here n is the hydration number, a parameter designating number of water molecules associated with each repeating unit of the polymer, M_0 and M_{H_2O} are the molecular weights of a repeating unit of the polymer and of water, respectively.

The DSC melting peak appeared around 0 °C is attributed to the melting of free solvent in the polymer solution; so ΔH_{m} obtained from the DSC melting curve should be written as:

$$\Delta H_{\text{m}} = \Delta H_{\text{m}}^{0} \cdot (1 - C_{\text{solvated}}) \tag{5}$$

Substituting Eq. (4) into Eq. (5) one gets:

$$\Delta H_{\text{m}} = \Delta H_{\text{m}}^{0} \cdot \left(1 - \frac{M_0 + n \cdot M_{H_2O}}{M_0}\right) \tag{6}$$

Then, the hydration number can be solved from Eq. (6) as

$$n = \left[\left(1 - \frac{\Delta H_{\text{m}}}{\Delta H_{\text{m}}^{0}}\right) \cdot \frac{1}{C} - 1\right] \cdot \frac{M_0}{M_{H_2O}} \tag{7}$$

3. Results and discussion

The DSC ice-melting diagrams of solutions with various concentrations for PVA I are shown in Fig. 1. The melting peak varies considerably with the concentration. The peak area decreases

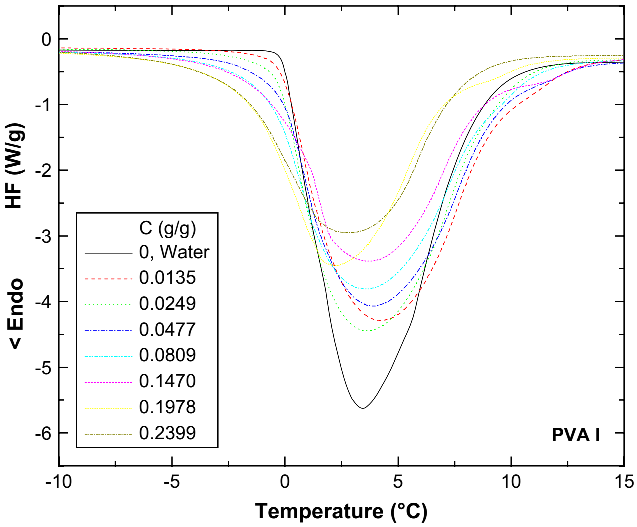

Fig. 1. DSC ice-melting diagrams of PVA I aqueous solutions with different concentrations.

Table 2
Hydration numbers of three PVA samples with various concentrations calculated from the variation of ice-melting enthalpies

PVA I			PVA II			PVA III		
C, g/g	H_m, J/g	n	C, g/g	H_m, J/g	n	C, g/g	H_m, J/g	n
0.00612	325.7	6.96	0.00808	323.2	6.94	0.00763	323.7	6.96
0.0135	316.3	6.88	0.0115	318.8	6.92	0.0160	315.8	5.68
0.0249	301.8	6.88	0.0177	310.9	6.93	0.0291	304.7	4.81
0.0477	279.1	5.93	0.0268	300.8	6.49	0.0492	296.8	3.03
0.0809	258.8	4.33	0.0355	292.6	6.00	0.0669	286.8	2.67
0.1245	225.4	3.92	0.0608	278.6	4.18	0.1020	264.4	2.53
0.1470	215.8	3.43	0.0870	259.0	3.83	0.1358	240.5	2.58
0.1978	199.6	2.52	0.1050	251.3	3.30	0.1817	209.9	2.55
0.2399	170.2	2.55	0.1574	225.0	2.61	0.2627	155.3	2.53
–	–	–	0.1854	207.5	2.54	–	–	–

with increasing concentration. These DSC endothermic peaks correspond to the ice melting of freezable water in solutions and can be used to calculate the hydration numbers. Meanwhile, the onset temperature of the melting peak which denotes the melting temperature of free water in PVA solution decreases with increasing concentration. The discrepancy of these temperatures to the melting point of pure water reflects the phenomenon of the melting point depression in PVA solutions. By the principle cited in the previous paragraph, the hydration number (n) of PVA I, PVA II and PVA III in solutions with various concentrations are calculated from the enthalpy (ΔH_m) and listed in Table 2.

In Fig. 2, the hydration number n of three PVA samples in water is plotted as function of concentration. It clearly demonstrates that in the range of concentration studied, the hydration number varies within two extremes, namely a higher value of $n = 7$ at a lower concentration and a lower value of $n = 2.5$ at a higher concentration. For a polymer with a given molecular weight, the hydration number changes from the value of 7 at low concentrations gradually to a plateau value of 2.5 as the concentration increases. It seems there exists a transition from a high hydration state ($n = 7$) at a lower concentration to a low hydration state ($n = 2.5$) at a higher concentration. Fig. 2 also shows that this transition is molecular weight dependent as the n–C curve shifts leftward as the molecular weight of PVA increases. These features could be more clearly demonstrated by a plot of n versus log C as shown in Fig. 3. The locations of the overlap concentration (C^*) estimated as the reciprocal of intrinsic viscosities of the three PVA samples are represented by vertical arrows with notation at the top of this diagram. In the diagram the C^* and C^*_{gel} of the sample used for studying hydrogel formation by freezing the solutions [18] are also indicated by dotted vertical lines. In addition, the data of hydration number of partially swollen PVA chemically cross-linked hydrogel reported earlier [15] are plotted in the same figure. Thus Fig. 4 represents the variation of the hydration number of PVA samples covering the whole concentration range.

In Fig. 3, it could be seen that the hydration number kept constant in a high level in the low concentration region. However, as the concentration increases to the overlap concentration, i.e., the reciprocal of intrinsic viscosity of the sample, the hydration number begins to fall gradually with increasing concentration until it reaches another hydration state. Since the overlap concentration is molecular weight dependent, the variation of hydration number with concentration is also diverse and depends on molecular weight of the sample. Therefore the transition region of hydration states may include a wide concentration range and depends on the molecular weight distribution of the sample. The overlap concentration of the sample solution used for studying freeze gel formation [18] is shown by dotted line in Fig. 3, which lies in the range of the present samples. However, the concentration at which the entire solution becomes a rigid gel upon freezing C^*_{gel} lies in the middle portion of the transition region. It suggests that the transition of hydration states is closely related to the crowding effect of polymer chains in solution.

In a previous paper [15] we have reported that as adding water to dry PVA hydrogel the hydration number of hydrogel increases from zero gradually to a limiting value of 2.5 as the gel approaching equilibrium swelling. This value is in well coincidence with that of the PVA solutions in the low hydration state.

The concentration dependent transition of hydration from one state to another may be treated mathematically by a quantitative

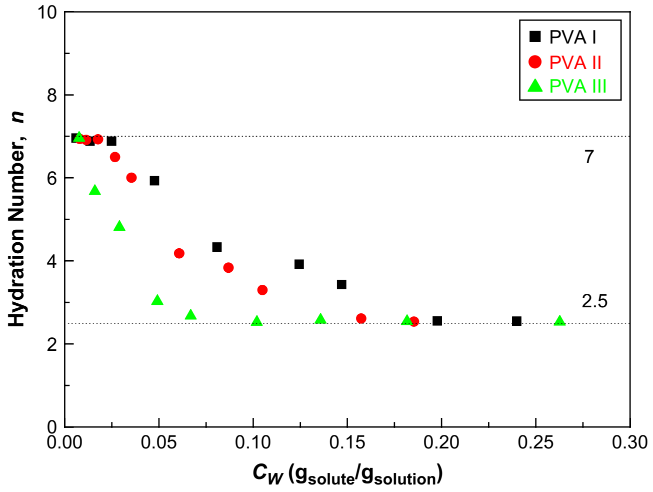

Fig. 2. The variation of hydration number with concentration of poly(vinyl alcohol) for three samples with different molecular weights.

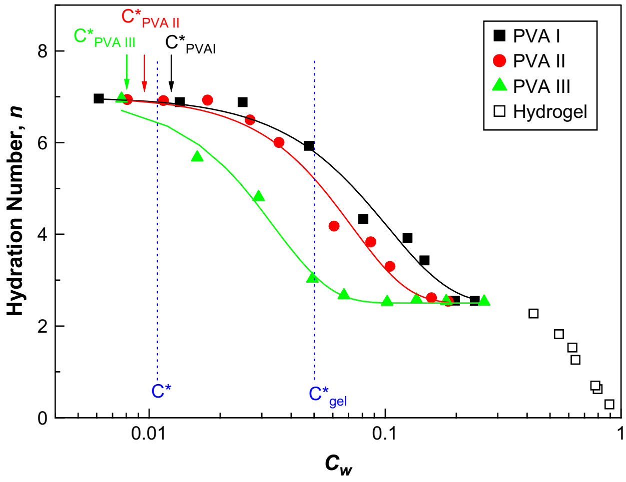

Fig. 3. The variation of hydration number of PVA covering the entire concentration range. The colored curves are the fitting curves by Eq. (10).

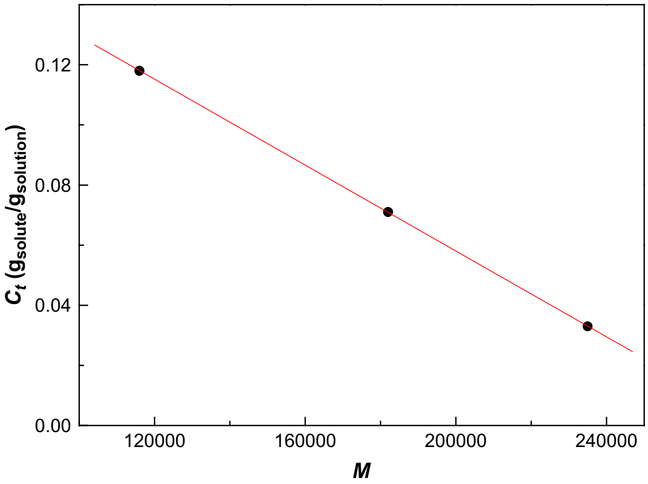

Fig. 4. The molecular weight dependence of transition concentration of hydration states of PVA.

formula involving two parameters in which one denotes the transition concentration and the other denotes the width of the transition region. For a simple transition, if the physical properties P measured at two concentration extremes of state A and B are denoted by P_A and P_B, respectively, then the properties measured at transition region should be concentration dependent and varies with concentration as $P(C)$. Then the properties of the polymer solution at the transition region may be written as

$$P(C) = w_A(C) \cdot P_A + (1 - w_A(C)) \cdot P_B \tag{8}$$

where $w_A(C)$ is the weight fraction of polymer in state A remaining at concentration C and $(1 - w_A)$ is the weight fraction of polymer in hydration state B. Solving for $w_A(C)$

$$w_A(C) = \frac{(P(C) - P_B)}{(P_A - P_B)} \tag{9}$$

Supposing the transition follows the rule of sigmoidal exponential decay

$$w_A(C) = e^{-(k \cdot C)^d} \tag{10}$$

where d denotes the width of the transition region and k is a constant denoting the transition concentration C_t as

$$C_t = \frac{1}{k} \tag{11}$$

The transition concentration C_t is defined as the concentration at which a fraction equals 0.632$(1 - 1/e)$ of the state at lower concentration regime transferred to a state at higher concentration regime.

Putting the two extreme hydration number $P_A = 7$ and $P_B = 2.5$ to fit the experimental data by Eq. (10), the parameters k and d of three PVA samples were evaluated as listed in Table 1. The fitting curves are in well coincidence with the experimental data as shown in Fig. 3.

The transition width parameter d varies around its mean value 1.7 which is reasonable because all the three PVA samples are purchased from different sources and possess different molecular weight distribution. The transition concentration $C_t(1/k)$ is linearly dependent on the molecular weight of PVA as shown in Fig. 4 and obeys the following relationship.

$$C_t = 0.2 - 7.14 \times 10^{-7} M \tag{12}$$

Polymer solution properties largely depend on the concentration regime it is located in [16,17]. The results obtained above clearly and undoubtedly indicate the existence of two hydration states for poly(vinyl alcohol) in the aqueous solution. The reason for the occurrence of such specific property is raised from the connectivity of polymer chains and the difference of concentration regimes. In the higher concentration region for a polymer like PVA, the chain segments are close to each other due to hydrophobic interaction and crowding effect. Two water molecules combine with the oxygen atom of the hydroxyl group of each repeating unit via hydrogen bonding in series and one additional water molecule bridges the already attached hydrated water molecules for intra- or inter-chain connection. On diluting the concentrated solution, intra- and inter-chain hydrated water connecting bridges break one by one and more water molecules add to the break points to form a clustered hydrated shell surrounding the main chain. Handa [19] produced hydrates of methane and ethane under pressure. He reported a hydration number of 6.00 ± 0.01 and 7.67 ± 0.02 for methane hydrate and ethane hydrate, respectively via DSC determination. The hydration number of 7 for each repeating unit of poly(vinyl alcohol) at dilute concentration regime deduced by the present work is in resemblance with that of methane and ethane hydrates.

Therefore, the transition of hydration states of polymer is merely a phenomenon associated with chain connectivity of the macromolecule and division of concentration regime of its solution. Poly(vinyl alcohol) is a typical water-soluble polymer. Its hydration behavior may be regarded as a model for both ionic and nonionic water-soluble macromolecules including polysaccharides, proteins, nucleic acids, etc. The present authors believe that the finding of the existence of two hydration states and the occurrence of a transition at certain concentration related to chain length should be a universal phenomenon for all water-soluble macromolecules.

4. Conclusions

1. The proposed principle for evaluating the hydration number of water-soluble polymer in solution is valid and easy to manipulate. The application of this principle to aqueous polyvinyl alcohol solution is successful.
2. The concentration dependency of hydration number demonstrates that the hydrated water-soluble polymer in solution exists in two distinct states; one state is fully hydrated with a higher hydration number which exists in the dilute concentration regime. The other exists in concentrated regime with a lower hydration number.
3. A transition occurs at the middle concentration portion of the two states which follows the rule of sigmoidal exponential decay with two parameters describing the transition concentration and the width of the transition region respectively.
4. The transition concentration lies at a concentration where $(1 - 1/e)$ portion of the highly hydrated state been transferred to the low hydrated state. This particular concentration is molar mass dependent in analogous to the overlap concentration which is just located on the onset point of the transition curve from the highly hydrated state.

Acknowledgments

Support of this research by the National Natural Science Foundation of China (No. 50633030) and the China Postdoctoral Science Foundation (No. 20070411036) is gratefully acknowledged.

References

[1] Wang Q, Cheng R. Polymer 1992;33:3978–80.
[2] Cheng R, Zhao S. ACS Symp Ser 1989;521:113–21.
[3] Cheng R, Yan X. Acta Polym Sinica 1989;6:647–54.

[4] Yang H, Cheng R, Xie H, Wang Z. Polymer 2005;46:7557–62.
[5] McBrierty VJ, Quinn FX, Keely C, Wilson AC, Friends GD. Macromolecules 1992;25:4281–4.
[6] Ahmad M, Huglin M. Polym Int 1994;33:273–7.
[7] Bastow TD, Hodge RM, Hill AJ. J Membr Sci 1997;131:207–15.
[8] McBrierty VJ, Martin SJ, Karasz FE. J Mol Liq 1999;80:179–205.
[9] Shibukawa M, Aoyagi K, Sakamoto R, Oguma K. J Chromatogr A 1999;832:17–27.
[10] Qu X, Wirsen A, Albertsson AC. Polymer 2000;41:4589–98.
[11] Hirata Y, Miura Y, Tanaka S, Nakagawa T. J Membr Sci 2000;176:21–30.
[12] Ping ZH, Nguyen QT, Chen SM, Zhou JQ, Ding YD. Polymer 2001;42:8461–7.
[13] Capitani D, Mensitieri G, Porro F, Proietti N, Segre AL. Polymer 2003;44:6589–98.
[14] Baba T, Sakamoto R, Shibukawa M, Oguma K. J Chromatogr A 2004;1040:45–51.
[15] Li W, Xue F, Cheng R. Polymer 2005;46:12026–31.
[16] Daoud M, Cotton JP, Farnoux B, Jannink G, Sarma G, Benoit H, et al. Macromolecules 1975;8:804–18.
[17] de Gennes PG. Scaling concepts in polymer physics. Ithaca, NY: Cornell University Press; 1979.
[18] Liu M, Cheng R, Qian R. J Polym Sci Part B Polym Phys 1995;33:1731–5.
[19] Handa YP. J Chem Thermodyn 1986;18:915–21.