HYDRODYNAMIC BEHAVIOUR OF AMYLOSE ACETATE IN SOLVENT–PRECIPITANT MIXTURES*

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Abstract—Viscosity measurements have been carried out on 12 amylose acetate fractions dissolved in (1) $43 \cdot 3$ per cent nitromethane: $56 \cdot 7$ per cent n-propanol (v/v; a θ-solvent mixture), (2) 50 per cent nitromethane: 50 per cent n-propanol (v/v), and (3) nitromethane. The following relations were obtained between limiting viscosity number and molecular weight: solvent (1), $[\eta] = 9 \cdot 16 \times 10^{-2} \bar{M}_w^{0 \cdot 50}$; solvent (2), $[\eta] = 1 \cdot 70 \times 10^{-2} \bar{M}_w^{0 \cdot 66}$; solvent (3), $[\eta] = 8 \cdot 50 \times 10^{-3} \bar{M}_w^{0 \cdot 73}$. The flexibility of the molecular coil in these three solvents is discussed, and the free-draining characteristics of the polymer are shown to be negligibly small.

INTRODUCTION

FEW NATURALLY occurring polymers have been investigated to the same extent as has cellulose and its derivatives. These investigations show that the cellulose molecule in solution is extended principally as a result of short-range interactions; i.e. the high exponents ($\sim 1 \cdot 0$) in the Mark–Houwink equation are a consequence of high chain stiffness.

This inherent stiffness of the cellulose chain is further emphasized by viscosity measurements carried out at the precipitation point, i.e. the Flory θ-point. For synthetic polymers, such measurements usually result in an exponent of $0 \cdot 50$ in the Mark–Houwink equation. This is not the case with the cellulose derivatives. For example, the exponent has a value of $0 \cdot 83$ for cellulose triacetate in a methylene chloride: ethanol precipitation mixture.[1] Values of $0 \cdot 5$ have been recorded for cellulose tributyrate in a dodecane: toluene mixture[2] and for cellulose tricaprylate in dimethyl formamide.[2] These measurements, however, were carried out at high temperatures (122° and 140°, respectively) at which the molecules are probably much more flexible than they are at room temperature.

Thus the cellulose derivatives generally do not show the expected behaviour at the precipitation point, unless high temperatures are involved. We now wish to present the viscosity behaviour of the analagous amylose triacetate derivative at its precipitation point.

EXPERIMENTAL

The fractionation of linear amylose and the subsequent conversion of the 12 fractions to the triacetates have been described in detail elsewhere.[3]

The method of Schultz and Flory[4] was employed to determine the θ-point in a mixture of nitromethane (solvent) and n-propanol (precipitant). Four polymer fractions of widely separated molecular weights (fractions 1, 5, 10 and 12) were used. Each was dissolved in nitromethane to give $0 \cdot 2$ per cent solutions. Two millilitres of each solution was equilibrated at 25° and n-propanol, also at 25°

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was added slowly, with stirring, until a permanent turbidity was observed. A measured aliquot of nitromethane (1–2 ml) was then added, and more n-propanol until the turbidity again appeared. The process was repeated until a value of $\sim 0\cdot 015$ per cent in concentration of amylose acetate was reached.

Measurements of limiting viscosity number were carried out at 25° in the θ-solvent, [solvent (1) in the following discussion], in a non-θ mixture of nitromethane and propanol, (50:50; v/v) [solvent (2)] and also in pure nitromethane [solvent (3)]. (Experimental details and the values for the nitromethane have been reported previously[3]). The molecular weights of the fractions were obtained from light scattering experiments carried out in nitromethane, as detailed by Banks, Greenwood and Hourston.[3]

RESULTS AND DISCUSSION

Composition of the θ-mixture

Figure 1(a) shows a graph of the volume-fraction of solvent at the precipitation point (v_1) as a function of the weight-concentration of amylose acetate (v_3) for the four fractions. The values of v_1 obtained by extrapolation to $v_3 = 0$ are shown as a function of $\bar{M}_w^{-0\cdot 50}$ in Fig. 1(b). The value of v_1 obtained by extrapolating to $\bar{M}_w^{-0\cdot 50} = 0$ is $0\cdot 436$. As emphasized by Schultz and Flory,[4] this particular method of extrapolation to infinite molecular weight is purely empirical. If $\bar{M}_w^{-1}$ rather than $\bar{M}_w^{-0\cdot 50}$ is used for the abscissa in Fig. 1b, a value of $v_1 = 0\cdot 430$ is obtained on extrapolation. In this work, the average of these values was used ($v_1 = 0\cdot 433$).
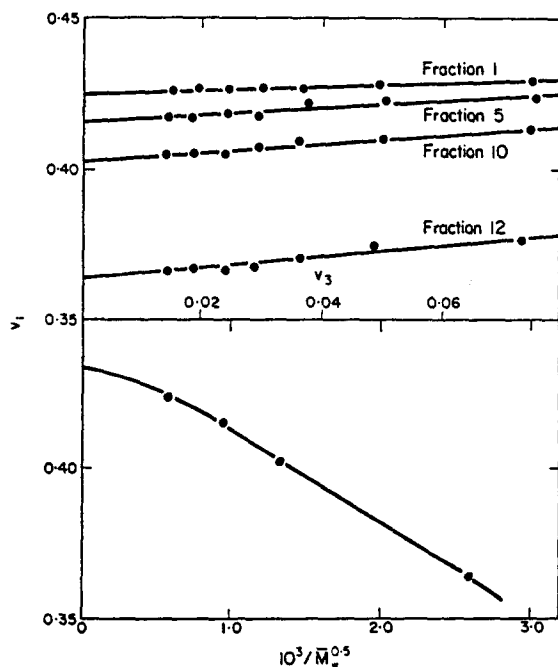

FIG. 1. (a) The volume-fraction of solvent at the precipitation point (v_1) as a function of the weight-concentration of amylose acetate (v_3); (b) Values of v_1 (when $v_3 = 0$) as a function of $\bar{M}_w^{0\cdot 5}$.

Fraction	$\bar{M}_w \times 10^{-6}$	$[\eta]_1{}^*$ (ml/g)	$[\eta]_2{}^\dagger$ (ml/g)	$[\eta]_3{}^\ddagger$ (ml/g)
1	3·11	168	334	475
2	2·17	135	261	365
3	1·68	121	215	300
4	1·34	110	187	255
5	1·09	97	164	225
6	0·869	86	138	185
7	0·818	82	134	178
8	0·755	81	128	170
9	0·676	77	120	155
10	0·569	69	106	133
11	0·376	56	81	100
12	0·148	35	44	51

* Measured in 43·3 per cent nitromethane/56·7 per cent n-propanol (θ-mixture).
† Measured in 50 per cent nitromethane/50 per cent n-propanol.
‡ Measured in nitromethane.

Limiting viscosity number/molecular weight relations

Table 1 records the limiting viscosity numbers measured in the three solvents, and also the molecular weights of the 12 fractions; Fig. 2 shows log $[\eta]$ as a function of log $\bar{M}_w$. Over the molecular weight range available, a linear relation is observed for each solvent i.e.

$$[\eta]_1 = 9·16 \times 10^{-2}\ \bar{M}_w{}^{0·50} \tag{1}$$

$$[\eta]_2 = 1·70 \times 10^{-2}\ \bar{M}_w{}^{0·66} \tag{2}$$

$$[\eta]_3 = 8·50 \times 10^{-3}\ \bar{M}_w{}^{0·73}. \tag{3}$$

The exponent of 0·50 for solvent (1) is the theoretical value for a Gaussian coil in a θ-solvent. Furthermore, as the nature of the solvent is improved by the progressive removal of precipitant, the value of the exponent increases. This is exactly the behaviour shown by the vast majority of vinyl polymers.[5]

It should be noted that the 43·3 per cent nitromethane/56·7 per cent n-propanol mixture is a true θ-solvent for amylose acetate in that a temperature-reversible precipitation occurs if the solution is cooled substantially below 25°. This is in strong contrast to the behaviour of native amylose in aqueous KCl where a viscosity exponent of 0·50 is observed over a temperature range of approximately 20°C.[6, 7]

The flexibility of the polymer coil

The value of 0·50 for the exponent in (1) indicates the flexible nature of the amylose acetate molecule for, under similar precipitation conditions, cellulose triacetate is so inherently stiff that a much higher exponent is observed. This increased flexibility must be due to the inter-glycosidic bond being alpha in character, amylose itself is much more flexible than is cellulose, as shown by the fact that both aqueous[6, 7] and non-aqueous[8] θ-solvents are known for the former. The only derivative of amylose which
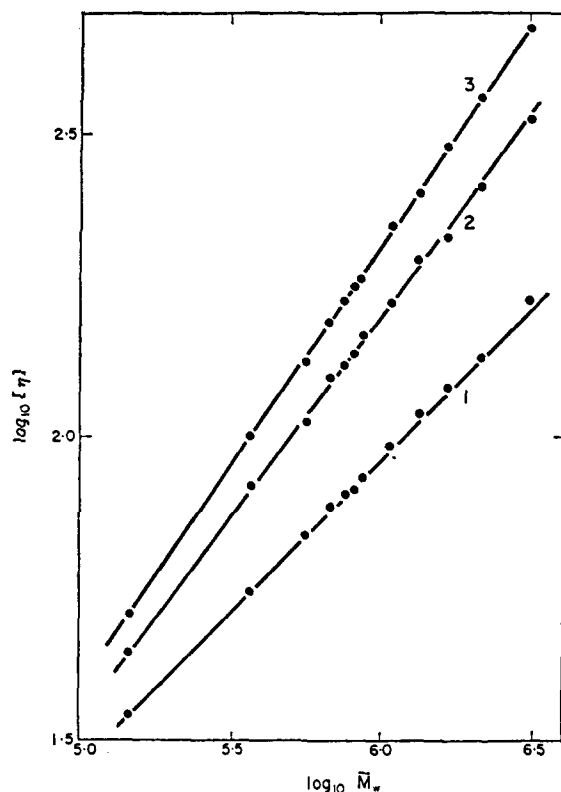
FIG. 2. Log$_{10}$ [η] as a function of log$_{10}$ $\bar{M}_w$ for the amylose acetate fractions dissolved in (1) nitromethane: propanol (θ-mixture), (2) nitromethane: propanol (50/50; v/v), (3) nitromethane.

is comparable in behaviour to the corresponding cellulose derivative is the tricarbanilate.[9] In this particular case, the high exponents observed for the macromolecule in various solvents have been shown to arise from the extension due to hindered rotation rather than to solvent effects. (It is reported that even at values of $\bar{M}_w$ of ~4 × 10^6, Gaussian statistics are not obeyed[9]). This hindered rotation must, from the evidence quoted above for the flexibility of amylose and its acetate, be due principally to the large size of the substituent carbanilate residues.

A measure of the flexibility of amylose acetate in the different solvents may be obtained from the Kuhn[10] statistical segment length, A_m, the value of which is inversely proportional to the flexibility of the coil. This parameter is shown in Table 2, and is compared with those from other studies on amylose acetate. All calculations were based on a bond length of 4·41Å for the extended glucose unit in the Cl conformation.[11]

Under θ-conditions, there are approximately 8 monomer units in each statistical segment. This value is similar to that for amylose in aqueous KCl (θ-solvent), where there are 6 residues.[7] For nitromethane, we find A_m to be 77Å. Sedimentation studies[3] yielded a rather lower value (A_m = 65Å). Thus there are 15–18 glucose

TABLE 2. THE KUHN STATISTICAL SEGMENT LENGTH FOR AMYLOSE ACETATE IN
VARIOUS SOLVENTS

Solvent	A_m (Å)	No. of monomer units statistical segment	Ref.
43·3 % nitromethane/56·7 % n-propanol	34	8	*
50 % nitromethane/50 % n-propanol	58	13	*
Nitromethane	78	18	*
Nitromethane†	110	25	(12)
Nitromethane	120	27	(13)

* This work.
† Cowie's results have been re-calculated using a bond length of 4·41 Å.

triacetate residues in each Kuhn statistical segment. The average value of 15 units is quite comparable to that observed for polystyrene in toluene,[10] where there are 13 styrene residues in each statistical segment. (The exponent of the Mark–Houwink equation for this system is ~0·7[14] very close to that reported here for amylose acetate in nitromethane).

The A_m values reported by Cowie[12] and by Patel and Patel[13] are mutually consistent, but higher than those found in this work. Indeed, these values might suggest that the amylose acetate chain is fairly inflexible. However, the value of A_m derived from Cowie's sedimentation studies[15] is 55Å, which is in agreement with our figure. Patel and Patel[13] state that their high value of A_m is in direct opposition to all their other conclusions, which suggest that amylose acetate is at least as flexible as polystyrene.

Partial free-draining in amylose acetate

Recently, Burchard[16] has suggested that draining effects in polysaccharides and their derivatives are not negligible. This is in contrast to the work of Kamide and Inamoto[17] on amylose in various solvents, and to sedimentation studies on amylose, [15, 18] where in neither case could any evidence of free-draining be detected.

As a measure of draining, Kamide and Inamoto[17] used the expression derived by Kamide and Kawai.[19] This is based on the Flory[5] treatment, i.e.

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

or

$$[\eta] = K_\theta M^{\frac{1}{2}}a^3,$$
(5)

and the Kurata–Stockmayer–Roig[20] expression for α

$$a^3 - a = C.g(a).z,$$
(6)

and yields

$$- \log K + 1·5 \log [1 + 4/3 \{(a - 0·5)^{-1} - 2\}^{-1}]$$
$$= (a - 0·5) \log M_0 - \log K_\theta,$$
(7)

where M_0 is approximated by the geometric mean of the molecular weight range over which K has been measured.

Alternatively, (4) and (5) may be used in conjunction with the Fixman[21] expression

$$a^3 = 1 + 1 \cdot 55z, \tag{8}$$

which gives

$$- \log \left[K\{1 - 2(a - 0 \cdot 5)\} \right] = (a - 0 \cdot 5) \log M_0 - \log K\theta. \tag{9}$$

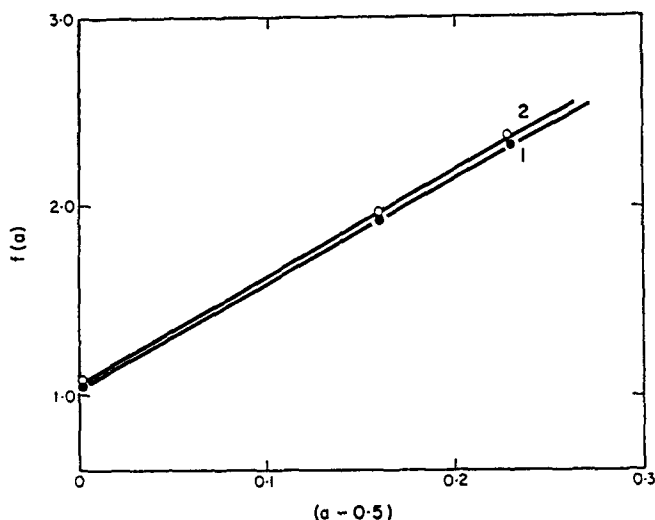Equation (9) has been derived independently by Kamide and Moore[22] and by Burchard.[16]

FIG. 3. $f(a)$ as a function of $(a - 0 \cdot 5)$; $f(a) = -\log_{10}[K\{1 - 2(a - 0 \cdot 5)\}]$ for curve 1, and $f(a) = -\log_{10}K + 1 \cdot 5 \log [1 + 4/3 \{(a - 0 \cdot 5)^{-1} - 2\}^{-1}]$ for curve 2.

If the left hand side of (7) or (9) is graphed against $(a-0 \cdot 5)$, a straight line will result only if the draining factor is negligible. In Fig. 3, the data are plotted according to (7) and (9). In both cases, the points fall on straight lines. Thus draining must occur in amylose acetate (in the molecular weight range $>1 \cdot 5 \times 10^5$) only to a negligibly small extent.

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Résumé—On a effectué des mesures de viscosité sur 12 fractions d'acétate d'amylose dissoutes (1) dans un solvant θ: mélange de $43 \cdot 3\%$ de nitrométhane et $56 \cdot 7\%$ de *n*-propanol (en volume) (2) dans un mélange 50 : 50 de nitrométhane et de *n*-propanol (en volume) (3) dans le nitrométhane. On a obtenu les relations suivantes entre les indices de viscosité limite et les masses moléculaires: solvant (1): $[\eta] = 9 \cdot 16 \times 10^{-2} \bar{M}_w^{05 \cdot 0}$; solvant (2): $[\eta] = 1 \cdot 70 \times 10^{-2} \bar{M}_w^{0 \cdot 66}$; solvant (3): $[\eta] = 8 \cdot 50 \times 10^{-2} \bar{M}_w^{0 \cdot 73}$. On examine les données sur la flexibilité de la pelote moléculaire et on montre que les caractéristiques de libre écoulement sont négligeables pour ce polymère.

Summario—Sono state fatte misure di viscosità su 12 frazioni di acetato di amilosio nei seguenti solventi: (1) $43 \cdot 3\%$ nitrometano: $56 \cdot 7\%$-propanolo (v'v solvente θ), (2) 50% nitrometano: 50% *n* propanolo (v'v), (3) nitrometano. Sono state ricavate le seguenti relazioni tra viscosità limite e peso molecolare: solvente (1) $[\eta] = 9 \cdot 16 . 10^{-2} M_w^{t \cdot 50}$, solvent (2) $[\eta] = 1 \cdot 70 . 10^{-2} M_w^{0 \cdot 66}$, solvente (3) $[\eta] = 8 \cdot 50 . 10^{-2} M_w^{0 \cdot 73}$. E' discussa la flessibilità delle molecole raggomitolate in questi tre solventi e viene mostrato che la permeabilità al solvente del polimero è molto piccola.

Zusammenfassung—An 12 Amyloseacetat-Fraktionen wurden Viskositätsmessungen durchgeführt in (1) $43 \cdot 3\%$ Nitromethan: $56 \cdot 7\%$ *n*-Propanol (v'v); ein θ-Lösungsmittelgemisch), (2) 50% Nitromethan: 50% *n*-Propanol (v'v), und (3) Nitromethan. Die folgenden Beziehungen zwischen Grenzviskosität und Molekulargewicht wurden erhalten: Lösungsmittel (1), $[\eta] = 9 \cdot 16 \times 10^{-2} \bar{M}_w^{0 \cdot 50}$; Lösungsmittel (2), $[\eta] = 1 \cdot 70 \times 10^{-2} \bar{M}_w^{0 \cdot 66}$;; Lösungsmittel (3), $[\eta] = 8 \cdot 50 \times 10^{-2} \bar{M}_w^{0 \cdot 73}$. Die Beweglichkeit des Molekülknäuels in diesen drei Lösungsmitteln wird diskutiert, und es wird gezeigt, daß der Durchspülungseffekt vernachlässigt werden kann.