

AMYLOSE TRIACETATE IN NITROMETHANE—THE SECOND VIRIAL COEFFICIENT*

W. BANKS and C. T. GREENWOOD

Department of Chemistry, The University of Edinburgh, Scotland

(Received 25 January 1968)

Abstract—The dimensionless parameter, $A_2\bar{M}_w/[\eta]$, has been obtained from measurements on amylose acetate fractions in nitromethane. These experimental results have been compared with various theoretical treatments. It has been shown that the semi-empirical equation of Krigbaum gives the best description of the experimental values. Furthermore, application of this theory gives a value for the unperturbed dimensions of amylose acetate in excellent agreement with those obtained from light-scattering and sedimentation measurements.

THEORIES developed to account for the values of the second virial coefficient, A_2 , of dilute polymer solutions are many in number, because of the different approximations introduced to deal with (a) *interchain* interactions, (b) *intrachain* interactions, and (c) the combination of (a) and (b). In this paper, we review these theories and apply them to the system of amylose acetate in nitromethane.

EXPERIMENTAL AND RESULTS

Linear amylose was isolated from potato starch and was subfractionated from dimethyl sulphoxide solution by the addition of butanol. The preparation of the acetate, and the physical measurements carried out on the fractions have been detailed elsewhere.^(1, 2)

TABLE 1. MOLECULAR PARAMETERS FOR AMYLOSE ACETATE FRACTIONS IN NITROMETHANE

Fraction	$\bar{M}_w \times 10^{-6}$	$A_2 \times 10^3$ (ml/g)	$(\bar{\rho}^2_g)_z^{1/2} \times 10^8$ (cm)	$[\eta]$ (ml/g)	$[\eta]_\theta$ (ml/g)
1	3.11	0.25	1070	475	168
2	2.17	0.25	860	365	135
3	1.68	0.24	735	300	121
4	1.34	0.22	645	255	110
5	1.09	0.24	570	225	97
6	0.869	0.24	500	185	86
7	0.818	0.24	485	178	82
8	0.755	0.25	465	170	81
9	0.676	0.25	435	155	77
10	0.569	0.24	390	133	69
11	0.376	0.25	310	100	56
12	0.148	0.25	180	51	35

$(\bar{\rho}^2_g)_z$ = Z-average mean square radius of gyration.

$[\eta]_\theta$ = limiting viscosity number measured in a θ -mixture of nitromethane and *n*-propanol (43.3:56.7; v/V).

Table 1 presents a summary of the experimental parameters used in this paper.

* This is Part 42 in the series "Physicochemical Studies on Starches".

DISCUSSION

(a) The molecular weight dependence of the virial coefficient, A_2

Figure 1 shows A_2 as a function of molecular weight. In the molecular weight range employed $[(0.15 - 3.1)10^6]$ there is virtually no change in the value of A_2 . According

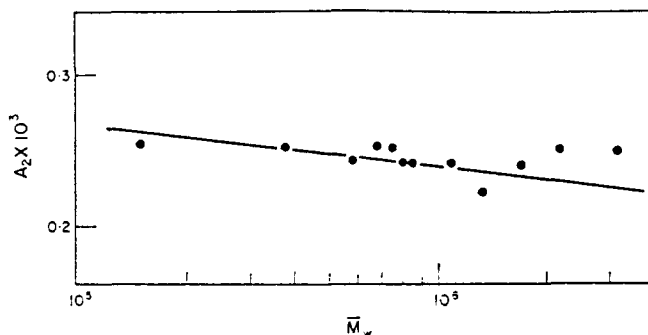


FIG. 1. A_2 as a function of molecular weight; ●, experimental values; —, line corresponding to a value of $\gamma = 0.05$ in Eqn. (1).

to the original lattice theory,^(3, 4) A_2 is indeed independent of molecular weight, but the more recent theories⁽⁵⁻⁷⁾ suggest a relation of the form

$$A_2 = \text{constant } M^{-\gamma},$$

where γ is a parameter the largest possible value⁽⁷⁾ of which is 0.15. Moreover, this value is attained only in the limiting case of extremely good solvents. Our earlier studies of the hydrodynamic behaviour of amylose acetate in nitromethane⁽¹⁾ show that this criterion is not satisfied, and a value of ~ 0.05 for the exponent in Eqn. (1) is probably to be expected. For the restricted molecular-weight range examined (covering slightly more than one order of magnitude), such a small variation in A_2 could easily be within experimental error. The line in Fig. 1 has been drawn assuming $\gamma = 0.05$, and only the values for the two highest molecular-weight fractions deviate from it to any considerable extent.

It should also be noted that many cellulose polymers are similar to amylose triacetate in having little dependence of A_2 on molecular weight.

(b) The second virial coefficient, A_2

In general, the theories for the second virial coefficient may be written in the form

$$A_2 = Y.F(X), \quad (1)$$

where Y is independent of molecular weight, but dependent on temperature. The function $F(X)$ decays monotonically from unity at $\alpha = 1$, where α is the Flory expansion factor. However, the exact form of the function $F(X)$ is as yet unknown and the various theoretical interpretations of this function are discussed below.

In terms of the Flory^(8,9) treatment, Y may be defined as

$$Y = \frac{1}{2} (1 - 2 \chi_1) (\bar{v}^2/V_1), \quad (2)$$

where χ_1 is a solvent-solute interaction parameter, \bar{v} is the partial specific volume of the polymer, and V_1 the molar volume of the solvent. Equation (2) may also be written in terms of the parameter, z , where

$$z = (\bar{v}^2/N_A V_1) (3/2 \pi)^{3/2} (1 - 2 \chi_1) M^{1/2} / (\bar{r}_0^2/M)^{3/2}. \quad (3)$$

Substitution of (3) in (2) gives

$$Y = \frac{1}{2} N_A (2 \pi/3)^{3/2} (\bar{r}_0^2/M)^{3/2} z M^{1/2}. \quad (4)$$

The relations $[\eta]_\theta = \phi (\bar{r}_0^2/M)^{3/2}$, and $[\eta]/[\eta]_\theta = \alpha_\eta^3$, then reduce (4) to

$$Y = (N_A/2\Phi) (2\pi/3)^{3/2} ([\eta]/M) (z/\alpha_\eta^3). \quad (5)$$

Substitution of (5) in (1) gives⁽⁷⁾

$$A_2 M / [\eta] = (N_A/2\Phi) (2\pi/3)^{3/2} (z/\alpha_\eta^3) F(X). \quad (6)$$

The function $F(X)$ was first obtained in a closed form by Flory and Orofino,⁽⁹⁾ who found the relation

$$F(X) = \ln[1 + (\pi^{1/2}/4) X] \cdot [\pi^{1/2} X/4], \quad (7)$$

where $X = 3^{3/2} z/\alpha^3$. (8)

To make use of (7) and (8), it is necessary to express α in an appropriate closed form. This may be done using the Flory⁽¹⁰⁾ relation

$$\alpha^5 - \alpha^3 = C_1 z \quad (9)$$

where $C_1 = 2.60$. Evaluation of (7) using (8) and (9) and substitution of this value in (6) gives the Flory-Krigbaum-Orofino relation

$$A_2 M / [\eta] = 4.14 \log [1 + 0.885 (\alpha^2 - 1)]. \quad (10)$$

The derivation of (10) assumes that $\Phi = 2.2 \times 10^{23}$ and that $\alpha_\eta = \alpha$.

Stockmayer⁽¹¹⁾ has criticised Eqns. (7) and (9) on the grounds that both fail to give the theoretical numerical factor of z when expanded in series for small z . To force agreement with the series expansion, it is necessary to multiply X by 2.49 in (7), and to use $C_1 = 1.276$. This then gives a modified form of (10), namely,

$$A_2 M / [\eta] = 1.65 \log [1 + 4.50 (\alpha^2 - 1)]. \quad (11)$$

The Flory theory is based on the model of the uniformly expanded chain having a spherically symmetrical distribution of chain elements about the molecular centre of mass. The derivation of (10) and (11) also assumes that the distribution of segments about the centre of mass is Gaussian in form. Ishihara and Koyama⁽¹²⁾ replaced this distribution function by the more exact sum of N different Gaussian functions, but the resulting form of $F(X)$ is only marginally different from (7). Casassa and Markovitz⁽¹³⁾ developed a second type of theory, again having the uniformly expanded chain model as its basis, but having a spherical distribution of segments about the locus of an initial interchain contact, and obtained

$$F(X) = [1 - \exp(-1.093X)]/1.093X. \quad (12)$$

Substitution of (8), (9) [with $C_1 = 1.276$] and (12) in (6) gives

$$A_2 M / [\eta] = 0.731 [1 - \exp \{-4.45 (\alpha^2 - 1)\}]. \quad (13)$$

Casassa,⁽¹⁴⁾ however, later modified this theory by replacing the X of (12) by X' where $X' = 3^{\frac{1}{2}} z / \alpha_2^3$. The uniform expansion approximation used in the derivation of the above theories replaces the original chain by an effective Gaussian chain with a bond length $b = \alpha_2 b_0$, where b_0 is the bond length of the polymer, and α_2 is an expansion factor. According to Flory, $\alpha = \alpha_n$, and the derivation of (12) assumes further that $\alpha = \alpha_2$. Recognizing that $\alpha \neq \alpha_2$, and assuming a relation between α_2 and z of the form

$$\alpha_2^5 - \alpha_2^3 = 2.043z, \quad (14)$$

(13) is modified to

$$A_2 M / [\eta] = 1.17 [(\alpha_n^2 - 1) / (\alpha_2^2 - 1)] \{1 - \exp [-2.78 (\alpha_2^2 - 1)]\}. \quad (15)$$

All the above theories are based on the "fifth-power law"—so-called because in the limit of high α , $\alpha^5 \propto z$ (see Refs. 9 and 14). However, the more recent theoretical treatments favour a "third power" relation between α (and α_n and α_2) and z . For example, Kurata and Stockmayer⁽⁷⁾ have suggested that the modified Casassa-Markovitz expression be combined with the relation

$$\alpha_2^3 - \alpha_2 = 2.043g(\alpha_2)z, \quad (16)$$

with $g(\alpha_2) = [4\alpha_2^2 / (3\alpha_2^3 + 1)]^{3/2}$. Further, an equation analogous to (16) may be written for α_n , the numerical coefficient being in this case 1.10. This leads to the relation (17)

$$A_2 M / [\eta] =$$

$$1.36 [g(\alpha_2) (1 - \alpha_n^{-2}) / g(\alpha) (1 - \alpha_2^{-2})] \{1 - \exp [-2.78 (1 - \alpha_2^{-2}) / g(\alpha_2)]\}. \quad (17)$$

Kurata *et al.*⁽¹⁵⁾ have also obtained a closed expression for $F(X)$ of the form

$$F(X') = \{1 - [1 + 0.131X']^{-7.39}\} / 0.973X', \quad (18)$$

which they suggest should be combined with the Fixman equation

$$\alpha_2^3 = 1 + 1.779z. \quad (19)$$

Substitution of (8), (18), (19), and the analogue of (19) for α_n in which the numerical factor of z is 1.55, in (6) yields

$$A_2 M / [\eta] = 0.940 [(1 - \alpha_n^{-3}) / (1 - \alpha_2^{-3})] \{1 - [1 + 0.384 (1 - \alpha_2^{-3})]^{-7.39}\}. \quad (20)$$

Ptitsyn⁽¹⁶⁾ has obtained for $F(X')$ the relation

$$F(X') = \{1 - [1 + 0.856X']^{-0.286}\} / 0.246X', \quad (21)$$

and a closed expression for α of the form

$$\alpha^2 = [3.68 (1 + 9.36z)^{\frac{1}{2}}] / 4.68. \quad (22)$$

The combination of (6), (8) and (22) yields

$$A_2 M / [\eta] = 3.26 \{1 - [1 + 0.476 \{(4.68 - 3.68 \alpha^{-2})^{\frac{1}{2}} - \alpha^{-3}\}]^{-0.2865}\}. \quad (23)$$

The derivation of (23) assumes that $\alpha = \alpha_n = \alpha_2$.

Krigbaum⁽¹⁷⁾ has suggested a semi-empirical relation

$$A_2 M / [\eta] = 2.17 (1 - \alpha_n^{-3}). \quad (24)$$

The numerical factor in (24) is slightly different from that obtained by Krigbaum. The difference arises as a result of taking $\Phi = 2.2 \times 10^{23}$ rather than 2.1×10^{23} . For consistency, the value of 2.2×10^{23} has been used in the derivation of all the foregoing equations. It should be noted that this value of Φ is used in conjunction with $[\eta]$ measured in ml/g.

Figure 2 shows a plot of the dimensionless parameter $A_2 \bar{M}_w / [\eta]$ as a function of $(\alpha_n^2 - 1)$ for the experimental values, and for those calculated using the various theoretical relations. The closest correlation between experiment and theory is obtained

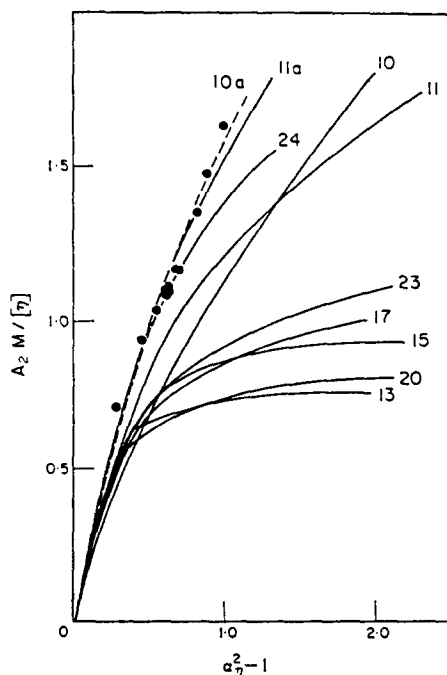


FIG. 2. $A_2 \bar{M}_w / [\eta]$ as a function of $(\alpha_n^2 - 1)$. Each line is numbered according to the theoretical relation from which it was constructed (see text); ●, experimental points; 10a is Eqn. (10) with $\Phi = 1.6 \times 10^{23}$; 11a is Eqn. (11) with $\Phi = 1.6 \times 10^{23}$.

using (24), i.e. the semi-empirical Krigbaum relation. In general form, there is also a reasonable correlation between the experimental curve, and those generated using (10) and (11)—particularly the former. The asymptotic limits obtained using the functions (13), (15), (17), (20) and (23) are not, in fact, observed experimentally.

It should also be emphasised that the viscosity constant Φ which appears in the factor Y (see Eqn. 5) may be treated as an adjustable parameter, in that its exact value is unknown. The value used here (2.2×10^{23}) is about the middle of the theoretical range— 1.6×10^{23} being the figure obtained using the Schulz⁽¹⁸⁾ treatment, and 2.8×10^{23} from the Kurata-Yamakawa⁽¹⁹⁾ theory, with various intermediate values. The experimental value of Φ for the system amylose acetate in nitromethane lies at the lower end of this range. If $\Phi = 1.6 \times 10^{23}$ is used in conjunction with (10),

the broken line in Fig. 2 results. There is in this case fairly good agreement with the experimental results. Use of this lower value of Φ increases the asymptotic limits of (13), (15), (17), (20) and (23), but the shapes of the curves generated by means of these equations are still completely different from that of the experimental curve.

The above theoretical treatments for the second virial coefficient all refer to monodisperse polymer systems. This criterion is not satisfied in the case of the amylose acetate fractions used here (in fact, $\bar{M}_w/\bar{M}_n \sim 1.5$), and therefore our conclusions regarding the fit of various theories to the experimental results must be regarded with some caution. However, the value of A_2 for the unfractionated parent polymer ($\bar{M}_w/\bar{M}_n \sim 2$) is 0.24×10^{-3} ml/g, which is very similar to the values for the fractions, suggesting that the effect of molecular weight distribution on A_2 is quite small. Fox *et al.*⁽²⁰⁾ have come to a similar conclusion whilst investigating the dilute solution properties of poly-(methyl methacrylate).

It should also be noted that the various functions $F(X')$ employed in the above theories may be generalized by⁽¹⁵⁾

$$F(X') = \left\{ [1 - (K_2/3^3)X']^{-(K_1 - K_2)/K_2} \right\} / [K_1 - K_2]X'/3^3 \quad (25)$$

with $K_1 = 5.68$ and K_2 treated as an adjustable parameter. Thus with $K_2 = 0$, (25) reverts to (12); with $K_2 = 4.41$, (21) is obtained.

(c) Determination of the unperturbed dimensions

The success of the Krigbaum⁽¹⁷⁾ theory in predicting the form of the experimental plot of $A_2\bar{M}/[\eta]$ as a function of α suggests that the same semi-empirical treatment of the light scattering data might be capable of giving an accurate measure of the unperturbed dimensions of amylose acetate. The basic relation from which (24) is derived is

$$(\bar{\rho}_g^2)^{\frac{1}{2}} = (\bar{\rho}_{g0}^2)^{\frac{1}{2}} + (3/N_A) (134/105) (1/4\pi)^{\frac{1}{2}} A_2 \bar{M}_w^{\frac{1}{2}} Q(h), \quad (26)$$

where $(\bar{\rho}_{g0}^2)^{\frac{1}{2}}$ is the mean-square unperturbed radius of gyration and $Q(h)$ is a heterogeneity factor. Re-arrangement of (26) gives

$$[(\bar{\rho}_g^2)_z/\bar{M}_w]^{\frac{1}{2}} = [(\bar{\rho}_{g0}^2)_z/\bar{M}_w]^{\frac{1}{2}} + (1.45 \times 10^{-25}) A_2 \bar{M}_w^{\frac{1}{2}} Q(h). \quad (27)$$

According to (27), a graph of $[(\bar{\rho}_g^2)_z/\bar{M}_w]^{\frac{1}{2}}$ as a function of $\bar{M}_w^{\frac{1}{2}}$ should yield a straight line relation having $[(\bar{\rho}_{g0}^2)_z/\bar{M}_w]^{\frac{1}{2}}$ as the intercept. This graph is shown in Fig. 3.

Reasonable linearity is observed over the entire molecular weight range. The intercept has a value of 0.076×10^{-24} cm³, from which $[(\bar{\rho}_{g0}^2)_z/\bar{M}_w]^{\frac{1}{2}} = 0.423 \times 10^{-8}$ cm. The more usual measure of unperturbed dimensions involves \bar{r}^2 , the mean square end-to-end distance of the polymer coil rather than $\bar{\rho}_g^2$, the radius of gyration. From the relation $\bar{r}^2 = 6 \bar{\rho}_g^2$, it follows that $[(\bar{r}_0^2)_z/\bar{M}_w]^{\frac{1}{2}} = 1.03 \times 10^{-8}$ cm. It is now necessary to convert the z -average value of \bar{r}^2 to the weight-average. Assuming that the distribution of molecular weights within the fractions is defined by the Schulz⁽²¹⁾ exponential function

$$w(M) = [y^{h+1}/\Gamma(h+1)] M^h \exp(-yM), \quad (28)$$

where $y = h/\bar{M}_n = (h+1)/\bar{M}_w = (h+2)/\bar{M}_z$, and $\Gamma(h)$ is the gamma function of h , then the heterogeneity correction is given by

$$[(\bar{r}_0^2)_z/\bar{M}_w]^{\frac{1}{2}} = [(h+2)/(h+1)]^{\frac{1}{2}} [(\bar{r}_0^2)_w/\bar{M}_w]^{\frac{1}{2}}. \quad (29)$$

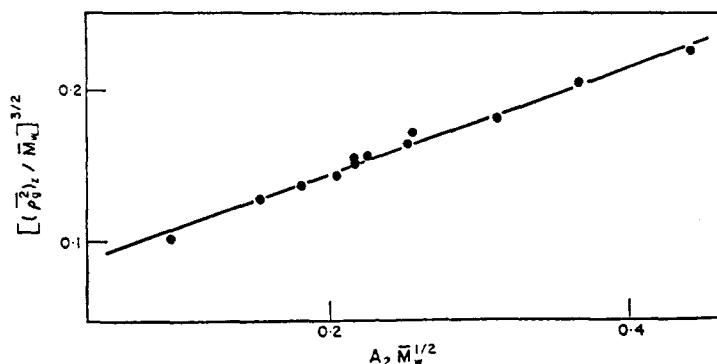


FIG. 3. $[(\bar{\rho}_g^2)_z / \bar{M}_w]^{3/2}$ as a function of $A_2 \bar{M}_w^{1/2}$.

As stated above, the fractions employed in this work are thought to have $\bar{M}_w / \bar{M}_n = 1.5$, from which $h = 2$. Thus $[(\bar{r}_0^2)_w / \bar{M}_w] = 895 \times 10^{-11}$ cm, in excellent agreement with our earlier values of 890×10^{-11} cm from light scattering studies, and 875×10^{-11} cm from sedimentation measurements.

The heterogeneity correction factor $Q(h)$ in (27) is given by

$$Q(h) = [(h+2)^{\frac{1}{2}} \Gamma(h+1)] / [(h+1)^2 \Gamma(h+2)]. \quad (30)$$

With $h = 2$, $Q(h) = 1.95$. Thus, from (27), the theoretical slope of the straight line shown in Fig. 3 should be 2.82×10^{-25} . In fact, the measured slope is 3.43×10^{-25} . Considering the nature of the approximations made in the derivation of (27), the agreement between the measured and theoretical values must be regarded as satisfactory.

Acknowledgements—This work was supported in part by a grant made by the U.S. Department of Agriculture under P.L. 480.

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Résumé—On a déterminé sur des fractions d'acétate d'amylose en solution dans le nitrométhane le paramètre sans dimensions $A_2M_w/[\eta]$. On confronte les résultats expérimentaux à différents traitements théoriques. On montre que c'est l'équation semi-empirique de Krigbaum qui rend le mieux compte des valeurs expérimentales. De plus, on tire de cette théorie une valeur des dimensions non-perturbées de l'acétate d'amylose qui sont en excellent accord avec celles déduites des mesures de diffusion de la lumière ou de sédimentation.

Sommario—E' stato determinato il parametro adimensionale $A_2M_w/[\eta]$, con misure su frazione di acetato di amilosio in nitrometano. I risultati sperimentali sono stati confrontati con diversi trattamenti teorici. Si è visto che l'equazione semiempirica di Krigbaum dà la migliore descrizione dei valori sperimentali. Inoltre con questa teoria si ottiene per le dimensioni imperturbate dell'acetato di amilosio un valore in eccellente accordo con quelli ottenuti da misure di diffusione della luce e di sedimentazione.

Zusammenfassung—Aus Messungen an Amyloseacetatfraktionen in Nitromethan wurde der dimensionslose Parameter, $A_2M_w/[\eta]$, ermittelt. Diese experimentellen Ergebnisse wurden mit verschiedenen theoretischen Ansätzen verglichen. Es wurde gezeigt, daß die halbempirische Gleichung von Krigbaum die experimentellen Werte am besten beschreibt. Außerdem ergibt die Anwendung dieser Theorie einen Wert für die ungestörten Dimensionen von Amyloseacetat, der mit den aus Lichtstreuungs- und Sedimentationsmessungen erhaltenen Werten ausgezeichnet übereinstimmt.