Viscosity–Temperature Relationships for Cellulose Acetate–Acetone Solutions

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Synopsis

Viscosity measurements were made for dilute solutions of three grades of cellulose acetate (acetyl content 39.8%, molecular weight $\bar{M}_v$ 30270 to 46250) in acetone in the temperature t range of 10° to 35°C. The data satisfied the Mark-Houwink equation, $[\eta] = K\bar{M}_v{}^\alpha$, where $[\eta]$ = limiting viscosity number and K and α are Mark-Houwink constants. The values of $[\eta]$ and α decreased with increase in temperature, and straight-line correlations were obtained for $-d[\eta]/dt$ versus $\bar{M}_v$ and log η versus $1/T$ (absolute temperature). The results are discussed in terms of solution properties of cellulose acetate in acetone and their possible relevance to reverse osmosis membrane science.

INTRODUCTION

In view of the extensive use of cellulose acetate and acetone in the formulation of casting solutions for making reverse osmosis membranes,[1] the solution properties of the above polymer–solvent system are of practical interest. Some of these properties have already been reported.[2] This paper is concerned with the viscosity–temperature relationships of dilute cellulose acetate–acetone solutions. Viscosities of dilute solutions of cellulose acetate and other cellulose esters have been studied before,[3–7] but the system cellulose acetate–acetone has not been examined in detail. The object of this paper is to study the viscosity–temperature data for the latter system in a manner similar to the work of Moore and co-workers[5–7] on dilute solutions of cellulose derivatives and interpret the data in terms of their possible relevance to reverse osmosis membrane science.

EXPERIMENTAL

Three grades of Eastman cellulose acetate[8] (acetyl content, 39.8%) designated as 398-3, 398-6, and 398-10, and "reagent" grade acetone (as obtained from the supplier) were used in these studies. The numbers 3, 6, and 10 included in the Eastman designations for the polymer refer to increasing viscosity grades represented by the drop times for standard falling-ball viscosity determinations. The above polymer samples were

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TABLE I
Densities of Cellulose Acetate–Acetone Solutions for Polymer
Concentrations of 0.25, 0.5, and 1.0 g/dl

Solution temp., °C	Solution density, g/cm³			
	0 g/dl	0.25 g/dl	0.5 g/dl	1.0 g/dl
10	0.8071	0.8081	0.8091	0.8111
15	0.8015	0.8025	0.8035	0.8055
25	0.7900	0.7910	0.7920	0.7940
30	0.7843	0.7853	0.7863	0.7883
35	0.7783	0.7794	0.7804	0.7824

the same as those studied before,[2] and their viscosity-average molecular weights ($\bar{M}_v$) were determined to be 30270, 34810, and 46250, respectively. Chromatographic analysis showed that the acetone used contained 0.11% water by volume.

Viscosity measurements were made in a Cannon-Ubbelohde number 75 dilution viscometer at 10°, 15°, 25°, 30°, and 35°C. The specified temperatures were maintained within 0.1°C. The maximum polymer concentration g used in the determination of limiting viscosity numbers [η] was 1.0 g/dl. Dilutions of the stock solutions were made in the viscometer, and three flow times consistent to 0.1 sec were obtained for each of a total of five concentrations for every polymer sample. The densities of cellulose acetate–acetone solutions were determined experimentally at each temperature for polymer concentrations of 0.25, 0.5, and 1.0 g/dl. These data are given in Table I. It was found that the solution densities for cellulose acetates of given extent of acetylation were constant at specified concentrations and independent of polymer molecular weight. The density data were used to calculate solution viscosity η (=viscometer constant × flow time × solution density).

RESULTS AND DISCUSSION

Data on Limiting Viscosity Numbers and Mark-Houwink Constants

The specific viscosities η_{sp} for each polymer were determined at the various temperatures in the usual manner[2] from the relative values of the viscometrically measured solution and solvent flow times. The plot of η_{sp}/g versus g was a straight line for each polymer and temperature studied. From the above plot, the limiting viscosity number [η] (= $\lim_{g \to 0} \eta_{sp}/g$) was obtained for each case. The Mark-Houwink equation, given as

$$[\eta] = K\bar{M}_v{}^{\alpha} \tag{1}$$

where K and α are empirical constants (Mark-Houwink constants), was found valid, as before,[2] for all the polymer samples and temperatures studied in this work. The values of [η], K, and α obtained in this work are given in Table II. The results showed that [η] decreased with increase

TABLE II
Data on Limiting Viscosity Numbers[a] and Mark-Houwink Constants

| | [η], dl/g | | | Mark-Houwink constants | |
Temp., °C	398-3	398-6	398-10	$K \times 10^4$, dl/g	α
10	0.946	1.049	1.265	4.00	0.752
15	0.872	0.972	1.195	4.04	0.747
25	0.815	0.906	1.111	4.46	0.731
30	0.810	0.896	1.100	4.71	0.722
35	0.770	0.874	1.041	5.09	0.711

[a] Of Eastman cellulose acetates 398-3, 398-6, and 398-10.
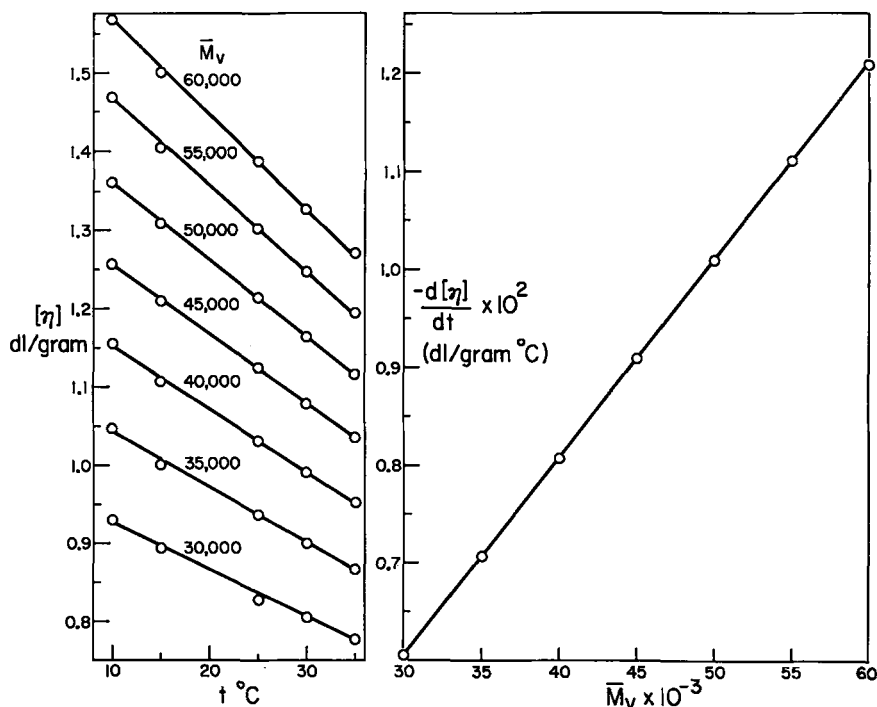

Fig. 1. Effect of temperature of solution and molecular weight of polymer on intrinsic viscosity.

in temperature for each polymer sample. Further, for the range of molecular weights of the polymer samples involved, the value of α decreased (with corresponding increase in the value of K) with increase in temperature. These results are generally similar to those reported for other cellulose derivatives in good solvents.[4–7]

Previous work[2] showed that the value of K and α remained constant for the cellulose acetate–acetone system at 25°C for the Eastman cellulose acetates (acetyl content, 39.4–39.8%) in the molecular weight range of 30,270 to 62,110. The values of K and α given in Table II may hence be

assumed valid for the same range of molecular weights for similar cellulose acetate polymers. Using the above values of K and α and eq. (1), intrinsic viscosities $[\eta]$ can be calculated as a function of temperature of solution and molecular weight of polymer. The results of such calculations are illustrated in Figure 1, which shows that, for the cellulose acetate-acetone system, the temperature t-versus-intrinsic viscosity $[\eta]$ correlation is a straight line with a negative slope the magnitude of which is a function of the molecular weight of the polymer. From the above correlation, the variation of $-d[\eta]/dt$ with molecular weight $\bar{M}_v$ of the polymer can be determined. The results of the latter calculations are also illustrated in Figure 1. which shows that $-d[\eta]/dt$ versus $\bar{M}_v$ is also a straight line and that the value of $-d[\eta]/dt$ increases with increase in molecular weight of the polymer. These results are strikingly similar to those reported by Flory et al.[4] and Moore and Brown[6] for cellulose acetate and ethyl cellulose polymers in different solvents.

Parameters of Viscous Flow

Moore and co-workers,[5-7] through their studies of the viscosity–temperature relationships of dilute solutions of several polymeric materials in a variety of solvents, have found that solution viscosity can be represented by an Arrhenius-type expression of the form

$$\eta = A \exp (Q/RT) \qquad (2)$$

in which the solution viscosity η is related to a preexponential term A and to the apparent activation energy of viscous flow of the solution, Q; R is the universal gas constant and T is the absolute temperature in this relationship. For a specified solvent, Q depends on the molecular weight $\bar{M}_v$ and concentration g of the polymer in solution according to the relationships

$$Q = Q_0 + k_e g \qquad (3)$$

and

$$k_e = K_e \bar{M}_v \qquad \quad ^\bullet (4)$$

where Q_0 is the activation energy of viscous flow of the pure solvent, k_e is a proportionality constant which depends on the solvent and on the polymer molecular weight, and K_e represents the contribution per unit polymer molecular weight and concentration to the apparent activation energy of viscous flow of the solution.

The preexponential term in eq. (2) is itself found to be an exponential function of molecular weight and concentration for stiff-chain molecules:

$$A = A_0 \exp (-k_a g) \qquad (5)$$

where k_a depends on the solvent and on $\bar{M}_v$, and A_0 is a constant for the pure solvent.

The foregoing equations imply that the correlations of $\ln \eta$ versus $1/T$, Q versus g, k_e versus $\bar{M}_v$, and $-\ln A$ versus g are straight lines. From the

TABLE III
Parameters of Viscous Flow

Polymer	$\bar{M}_v$	k_e, dl·kcal/ g-mole	k_a, dl/g	$K_e \times 10^5$ dl·kcal/ g-mole	$A_0 \times 10^4$, poise	Q_0, kcal/mole
398–3	30270	0.728	0.420	2.34	1.80	1.72
398–6	34810	0.815	0.467	2.34	1.80	1.72
398–10	46250	0.985	0.755	2.34	1.80	1.72
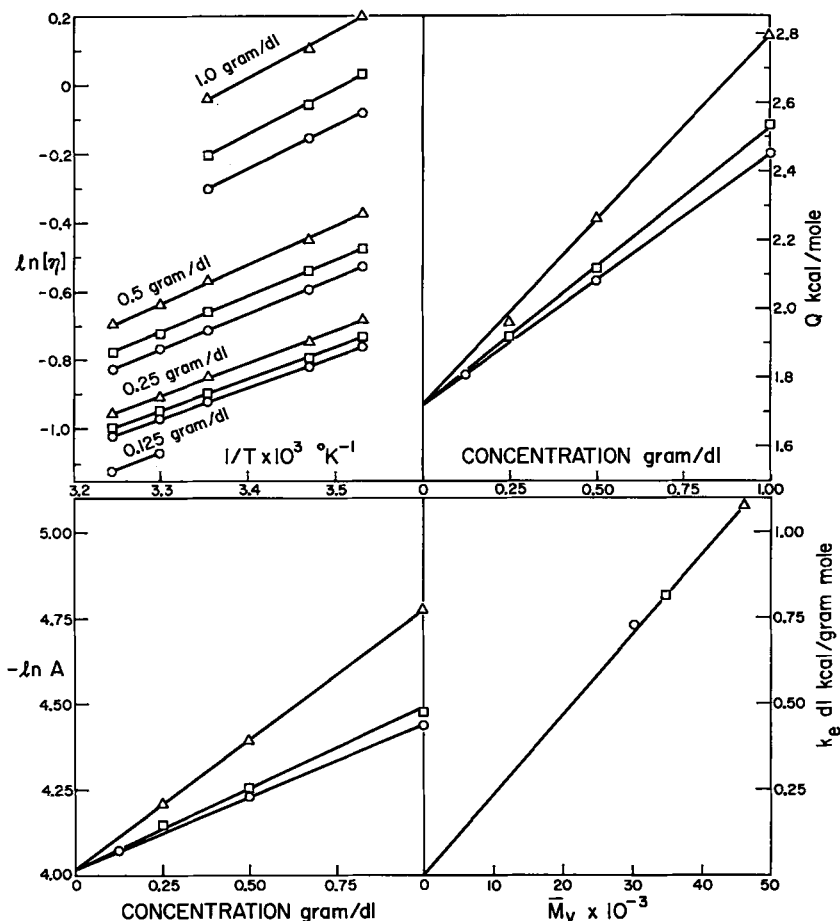
Fig. 2. Correlations of parameters of viscous flow for cellulose acetate–acetone solutions. Polymers: (⊙) 398-3; (□) 398-6; (△) 398-10.

experimental viscosity–temperature data obtained in this work, the above correlations were tested. The results, given in Figure 2, show that eqs. (2) to (5) represent well the viscosity–temperature data obtained for the cellulose acetate–acetone solutions studied in this work. The values of the parameters obtained from Figure 2 are summarized in Table III.

The activation energy of 1.72 kcal/mole for Q_0 obtained in this work compares well with the values of 1.70 kcal/mole given by Barrer[9] and 1.75 kcal/mole given by Fort et al.[10] for pure acetone. For cellulosic materials, K_e has been found to be positive and relatively constant for a variety of derivatives in most common solvents,[5,7] and the value of 2.34×10^{-5} dl·kcal/g-mole obtained here for cellulose acetate in acetone correlates well. Most common (noncellulosic) polymer–solvent systems exhibit a K_e that can be either positive, zero, or negative, but whose magnitude is likely to reach only 1–10% of that of a cellulose derivative. This is often considered to be additional support for the existence of cellulose acetate as stiff, extended entities in solution.[10]

The constants k_e and k_a determine the effect of concentration on Q and A, respectively. Their magnitudes are generally similar to other cellulosic materials although the k_e value for cellulose acetate is about twice that of cellulose nitrate in acetone,[7] indicating a greater concentration effect on the activation energy of viscous flow. Since k_e is related to $\bar{M}_v$ by the proportionality constant K_e in eq. (4), the effect of the molecular weight as well as the concentration of cellulose acetate will be more pronounced than for other cellulose derivatives and of course more pronounced than for noncellulose materials.

Significance of Above Results

The tendency of the Mark-Houwink constant α to decrease with increase in temperature, the large negative temperature coefficient for intrinsic viscosity, and the identity of the form of the viscosity–temperature relationships illustrated above for the cellulose acetate–acetone systems show that the discussions of Flory et al.[4] and Moore and co-workers[5–7] based on similar results are applicable to the structure of the cellulose acetate–acetone solutions studied in this work. Based on their discussions,[4–7] the following statements can be made with reference to the structure of dilute solutions of cellulose acetate in acetone. From hydrodynamic considerations of $[\eta]$ and other parameters of viscous flow, the molecules of cellulose acetate in acetone are characterized by high chain rigidity. This characteristic is also supported independently by electro-optical properties of cellulose esters in solution.[11] The influence of temperature on intrinsic viscosity can be ascribed primarily to changes in chain flexibility. The chain stiffness decreases as temperature increases. The cellulose acetate–acetone system is also characterized by high extensions of the polymer chain solution. The decrease in α with increase in temperature suggests decreasing chain extension with increase in temperature. The negative temperature coefficient of intrinsic viscosity is primarily due to a decrease in the value of $(\bar{r}_0^2 \bar{M}_v)$, where $\bar{r}_0^2$ is the mean square unperturbed end-to-end distance of the polymer chain in solution[6] and $\bar{M}_v$ is the average molecular weight of the polymer. Consequently, the end-to-end distance and hence chain extension decrease as the temperature increases for solutions of cellulose acetate in acetone.

Application of Coagulation Theory of Polymer Dispersion

A theory for the coagulation of polymer dispersions in solution has recently been presented by Rudin and Johnston.[12] This theory is strictly applicable to flexible, spherically swollen monodisperse polymers in solution. However, the application of this theory to the data of cellulose acetate–acetone systems studied in this work may be expected to indicate the general effects of temperature on the size of equivalent spherical polymer particles and the relative probability of collision between such particles resulting in polymer aggregation in solution. For the calculation of such particle size and probability, the following are the pertinent equations taken from the original paper of Rudin and Johnston.[12]

At any concentration, the volume fraction ϕ of polymer is given by

$$\phi = \frac{gN_0 v\epsilon}{M} \tag{6}$$

where g is the concentration (g/cm^3), N_0 is Avogadro's number, M is polymer molecular weight (taken as $\bar{M}_v$ in this wok), v is the volume (cm^3) of an unsolvated polymer molecule, and ϵ is an effective volume factor (dimensionless) to allow for swelling of the polymer by the liquid medium. The effective volume factor ϵ decreases with increase in concentration and ranges between ϵ_0 when g approaches zero and ϵ_x when g approaches a limiting concentration g_x. The volume fraction of swollen polymer, ϕ_x, at the limiting concentration g_x is taken to be 0.507 as in the original paper.

If the density of the amorphous polymer at the experimental temperature is ρ ($= 1.3$ g/cm³ in this work[8]), v is defined as

$$v = \frac{M}{\rho N_0} \frac{cm^3}{molecule} \tag{7}$$

so that

$$g_x = \frac{0.507\rho}{\epsilon_x}. \tag{8}$$

For a polymer of molecular weight M,

$$\epsilon_0 = \frac{KM^\alpha \rho}{2.5} \tag{9}$$

and

$$\epsilon_x = 2.6 + (1.7 \times 10^{-4})Z \tag{10}$$

where Z is the number of main chain atoms in the polymer molecule. Since the application of the foregoing equations to rigid cellulose acetate polymers can only be expected to give comparative results, it is assumed here that the effect of Z on the value of ϵ_x is small, and hence the latter is approximated as 2.6. At any concentration g, the effective volume factor ϵ is given by

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0} + \frac{g}{g_x}\left(\frac{\epsilon_0 - \epsilon_x}{\epsilon_0 \epsilon_x}\right). \tag{11}$$

TABLE IV
Effect of Temperature on Properties of Cellulose Acetate–Acetone
Solutions for Polymer Concentration of 1 g/dl

Temp., °C	a, Å	ϵ_0	ϵ	ϵ/ϵ_0	$1/(v\epsilon)^2 \times 10^{35}$, $(mole/cc)^2$
		Av. molecular wt. of polymer:	30,250		
10	64.23	48.73	28.67	0.5883	8.132
15	63.72	46.74	27.99	0.6114	8.532
25	62.91	43.75	26.93	0.6155	9.217
30	62.43	42.10	26.33	0.6254	9.642
35	61.98	40.62	25.76	0.6342	10.07
		Av. molecular wt. of polymer:	46,250		
10	78.22	67.02	33.89	0.5057	2.493
15	77.67	64.15	33.17	0.5171	2.602
25	76.72	59.64	31.97	0.5360	2.801
30	76.16	57.18	31.28	0.5470	2.926
35	75.61	54.91	30.61	0.5575	3.056

The probability p of permanent collision of two polymer particles in solution is directly proportional to the attractive interaction energy between the particles when they are in contact with each other. This interaction energy is proportional to the inverse sixth power of the distance between the centers of masses, and hence to the inverse sixth power of the diameter of uniform solvated polymeric spheres. Since the volume of a swollen spherical polymer particle is given by

$$\tfrac{4}{3}\,\pi a^3 \;=\; v\epsilon \tag{12}$$

where a is the radius of the polymer particle,

$$a^6 \;=\; \left(\frac{3v\epsilon}{4\pi}\right)^2 \tag{13}$$

consequently,

$$p \;\propto\; 1/(v\epsilon)^2. \tag{14}$$

The quantity $1/(v\epsilon)^2$ may hence be considered as a relative probability parameter for particle aggregation in the polymer solution.

Table IV gives numerical data on the effect of temperature on particle radius a, effective volume factors ϵ_0 and ϵ, and the relative probability parameter for particle aggregation $1/(v\epsilon)^2$ as a function of temperature for two polymer molecular weights at a polymer concentration of 1 g/dl. These data were obtained by using eqs. (7) to (13) and the values of K and α obtained in this work. In view of the limitations on the applicability of the theory for solutions of cellulose acetate polymers, the values of the parameters given in Table IV should be considered on a relative rather than an absolute basis.

The results show that the particle radius a decreases with increase in temperature; this is consistent with the statement made earlier that the polymer chain extension decreases with increase in temperature. The quantity ϵ/ϵ_0 is a measure of the swelling ratio of the polymer in the solvent. The results show that the swelling ratio increases with increase in temperature even though the value of each of the corresponding quantities ϵ_0 and ϵ decreases. The reason for this is understandable. With increase in solution temperature, the polymer particle is subject to two opposing changes, namely, a decrease in radius of gyration reflected in the changes in K and α (which is possibly caused by disolvation[13] of the ether linkages) and an increase in radius of gyration due to normal thermal expansion of the polymer. Thus, while the value of ϵ_0 (corresponding to zero polymer concentration in solution) is a function of K and α only, the value of ϵ is a function of the polymer concentration also. Consequently, the effect of temperature is greater on the value of ϵ_0 than on that of ϵ. The data in Table IV on particle radius and swelling ratio together indicate that the number of supermolecular polymer aggregates is increased with increase in solution temperature and decreased with increase in polymer molecular weight. The data on $1/(v\epsilon)^7$ show that the probability of permanent collision of polymer particles increases by about 25% by increase of solution temperature from 10° to 35°C; further, at a given solution temperature, the above probability decreases by a factor of more than 3 by increasing the molecular weight of the polymer from 30,250 to 46,250. These results are again consistent with the effect of temperature and molecular weight on the number of polymer particles in solutions.

CONCLUSIONS

The governing significance of solution structure in the mechanism of pore formation and development in the process of casting reverse osmosis membranes has been extensively discussed and illustrated with particular reference to casting solutions involving cellulose acetate (Eastman 398-3) and acetone.[14–16] In the light of these discussions, the effects of temperature variation on solution properties of cellulose acetate–acetone systems studied above seem particularly relevant. A greater flexibility for the polymer chain indicates a lesser extent of polymer solvation, and hence this can contribute to a higher evaporation rate constant for the solvent since more free solvent molecules are near the air–solution interface. A decrease in chain extension can contribute to a decrease in the size of supermolecular polymer aggregates in the casting solution. The coalescence of a concentrated polymeric casting solution follows the general rules of coagulation kinetics.[12] In the process of membrane formation, as solvent evaporates from the surface layer of a thinly spread viscous cellulose acetate casting solution, the resulting higher concentration of smaller coagulating species favors droplet coalescence in the interdispersed phase. The performance of cellulose acetate membranes has been shown[15,16] to be con-

sistent with all the above changes as a consequence of an increase in the temperature of the casting solution. Thus, the kind of data presented in this work has relevance to reverse osmosis membrane science, and hence such data can offer a useful basis in studies on reverse osmosis membrane development.

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