

Viscometric Behavior of Concentrated Cellulose Acetate Solutions

H. KIRK JOHNSTON, *Canada Centre for Inland Waters, Burlington, Ontario, Canada*, and S. SOURIRAJAN, *Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9*

Synopsis

The viscometric behavior of concentrated cellulose acetate solutions in a variety of solvent and mixed solvent systems has been studied. Rapid increases in solution viscosity with increase in cellulose acetate concentration are apparently related to polymer nonsphericity and the tendency of molecules to experience extensive nonhydrodynamic interactions. By employing a well-defined polymer solution theory in conjunction with an empirically determined calibration curve, accurate predictions of concentrated cellulose acetate solution viscosities are possible.

INTRODUCTION

Solution properties of normal polymeric species are adequately defined and understood in terms of well-characterized theories. Most polymers exist in solution as flexible, solvated spheres or helices which can be described by various physicochemical parameters in both dilute and concentrated solutions. General behavioral relationships are consistent for a wide variety of such materials over most useful ranges of concentrations. Cellulose and cellulose derivatives, however, often behave quite unlike most normal polymers in solution. Most of these differences can be related in part to the fact that the basic cellulosic chains exist in solution as rigid extended entities, and as such interact quite differently than flexible spheres or helices. This paper attempts to establish some general relationships to permit the prediction of certain physical properties and behavioral characteristics of concentrated cellulose acetate solutions in a variety of solvent and mixed solvent systems.

Solutions of cellulose acetate exhibit many characteristics which are generally shared by other cellulose derivatives. With an increase in solution temperature, the corresponding decreases in viscosity η and limiting viscosity number $[\eta]$ are characterized by an increase in K and a reduction in α in the Mark-Houwink expression

$$[\eta] = KM^\alpha \quad (1)$$

This tendency is consistent with the cellulose derivatives which have been examined^{2,3} but is the exact opposite from most other noncellulosic

polymer-solvent pairs. The apparently anomalous temperature behavior of cellulose systems is explained on the basis of reduced chain solvation at high temperatures.^{1,2,4,5} The resulting greater chain flexibility under such conditions permits a reduction in the macromolecular extension and a decrease in aggregate size.

The increase in viscosity with concentration for cellulosic solutions is found to be very nonlinear and to increase much more rapidly than would be expected from normal solution theory.^{6,7} Since cellulose acetate solution viscosities of a particular sample depend not only on the degree of acetylation but also very specifically on the source of the cellulose from which the derivative is prepared,⁸⁻¹⁰ it is common practice to characterize such samples according to their false viscosity. This characteristic represents the higher viscosity of a concentrated acetate solution compared to a standard cellulose acetate made from cotton linters and having the same limiting viscosity number. The false viscosity number has been defined in several ways, all of which attempt to adequately convey these unusually high experimental viscosities. As an example, a false viscosity number may be defined⁸ as one less than the ratio of the rate of change in viscosity with limiting viscosity number for a given cellulose acetate compared to the rate of change in viscosity with limiting viscosity number for a standard cotton linters acetate. Since cellulose is a natural polymer, such non-uniform behavior is not totally unexpected. Nonetheless, the magnitude of these effects is quite substantial and only further complicates attempts to explain the behavior of cellulose acetate in a predictable and completely consistent manner.

In the current study, a basic theory of polymer solutions⁷ was employed in an attempt to explain the behavior of cellulose acetate in various solvent and mixed-solvent systems. Although the correlations between predicted and experimental viscosities became progressively less precise as polymer concentration increased, it was found that an empirical calibration curve could be obtained which would permit an accurate estimation of solution viscosity for a given polymer in any solvent up to relatively high concentrations. Experimental reference to a standard such as cotton linters is not required in this approach. The method devised is likely applicable to other cellulosic derivatives.

EXPERIMENTAL

The Eastman cellulose acetates employed in this study were type E-398-3 with acetyl content 39.8%. Viscosity-average molecular weights were determined¹¹ to be 30270 and 27350 using the appropriate Mark-Houwink constants¹ of $K = 4.46 \times 10^{-4}$ dl/g and $\alpha = 0.731$ for cellulose acetate in acetone at 25°C. The solvents used were A.C.S. and C.P. solvents, except for acetone which was reagent grade, consistent with the previous work.¹ The mixed-solvent systems employed were denoted solvent I and solvent II and consisted of those constituents which were

used in the casting formulations for reverse osmosis membranes, type NRC 316¹⁶ and type NRC 316/ether.¹⁷ Their compositions by weight were as follows: solvent I—acetone, 69.2; water, 12.35; and magnesium perchlorate, 1.45; solvent II—acetone, 64.2; ethyl ether, 5.0; water, 12.35; and magnesium perchlorate, 1.45.

Viscosity measurements were performed at $25.0 \pm 0.01^\circ\text{C}$ in calibrated Cannon-Ubbelohde dilution viscometers. The viscometer constants for dilute and concentrated solution measurements ranged between 0.00425 and 0.1098 centistokes/sec, respectively. Dilutions were made in the viscometers for stock solutions of 0.50 g/dl or less. Solutions of higher concentrations were prepared as required and were not diluted. Flow times for solutions ≤ 2 g/dl were reproducible to within 0.1 sec, but measurements of concentrated solution (> 8 g/dl) flow times were not repeated because of the long times involved.

Mathematical calculations were carried out on an I.B.M. 360 computer.

RESULTS AND DISCUSSION

Cellulose and cellulose derivatives in solution exist as extended loops or spirals because of their relatively high rigidity. Indeed, solutions of moderate molecular weight celluloses are often considered rod-like in nature.¹² Such particles cannot be moved about in solution as easily as if they were compact spheres, thus their viscosity is much higher than the viscosity of spherocolloids. This phenomenon has been interpreted in terms of the molar frictional coefficient of the solution which attributes the high viscosity to the combined effects of shape and solvation. It is possible to predict the viscosity of spherically swollen monodisperse polymers in solution by applying the coagulation theory of Rudin and Johnston.^{6,7} The present study has shown that this theory may be extended and used in conjunction with an empirical calibration curve to permit the accurate prediction of cellulose acetate solution viscosities up to concentrations of 25 g/dl.

Solution viscosity η has been shown to be adequately represented by the following series equation^{6,13} for most common polymer-solvent systems:

$$\eta_0/\eta = 1 - 2.5\phi + 11\phi^5 - 11.5\phi^7 \quad (2)$$

where η_0 is the solvent viscosity and the volume fraction ϕ of polymer in solution is defined as⁶

$$\phi = \frac{gN_0v\epsilon}{M} = \frac{g\epsilon}{\rho} \quad (3)$$

where g is the polymer concentration (g/cm^3), N_0 is Avogadro's number, M is the viscosity-average molecular weight, v is the volume ($\text{cm}^3/\text{molecule}$) of an unsolvated polymer molecule ($v = M/\rho N_0$), ρ is the amorphous polymer density (g/cm^3), and ϵ is the effective volume factor (dimensionless) to allow for swelling of the polymer by the liquid medium. The

effective volume factor 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 polymer⁶ ϕ_x is 0.507 at the limiting concentration g_x , defined as

$$g_x = 0.507 \rho / \epsilon_x. \quad (4)$$

For a polymer of molecular weight M , ϵ_0 has been determined⁶ to obey the relationship

$$\epsilon_0 = \frac{KM^\alpha \rho}{2.5} \quad (5)$$

where K and α are the constants in the Mark-Houwink expression for the particular polymer, solvent, and temperature. The effective volume factor at the critical concentration ϵ_x is approximated as 2.60 for cellulose acetate solutions.¹ At any concentration g , the corresponding volume factor is given by

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0} + \frac{g}{g_x} \left[\frac{\epsilon_0 - \epsilon_x}{\epsilon_0 \epsilon_x} \right] \quad 0 < g \leq g_x. \quad (6)$$

Knowing the Mark-Houwink constants and the polymer molecular weight, concentration, and density, it is thus possible to accurately predict the viscosity of most common concentrated polymer solutions.⁶

The effective volume factor ϵ can be used to determine a , the radius of the equivalent swollen spherical particle in solution according to the equation

$$a = \left(\frac{3v\epsilon}{4\pi} \right)^{1/3}. \quad (7)$$

The particle radius so calculated can be incorporated into the Einstein-Stokes relation for the diffusion coefficient D of such a spherical particle diffusing in a liquid medium of viscosity η :

$$D = \frac{RT}{6\pi\eta N_0 a} \quad (8)$$

where R is the universal gas constant and T is the temperature in degrees Kelvin. The η and a values determined from eqs. (1) and (7) permit accurate prediction of dilute solution diffusion coefficients for a very wide variety of polymer-solvent systems.¹⁴ Solutions of cellulose acetate, however, exist in the form of inflexible rods and consequently deviate strongly from predicted diffusion and viscosity behavior, even at low concentrations. Such behavioral anomalies of cellulose derivatives have been interpreted in terms of the molar frictional coefficients of the species in solution, and attempts have been made to correlate the effects of shape and solvation¹⁵ with solution properties.

Molar frictional coefficients f are defined^{18,19} in terms of their solute/solution diffusion coefficients:

$$f = RT/D. \quad (9)$$

In an attempt to make the relative effects of shape and solvation on solution properties more explicit, specific frictional coefficients are defined as follows: f_0 = molar frictional coefficient for unsolvated spherical particles at infinite dilution; f_s = molar frictional coefficient for swollen spherical particles at the specified concentration in the defined solvent; f_T = molar frictional coefficient for swollen nonspherical particles at the specified concentration in the defined solvent.

From eqs. 7, 8, and 9, these molar frictional coefficients can be represented as

$$f_0 = 6\pi\eta_0 N_0 \left(\frac{3v}{4\pi} \right)^{1/3} \quad (9a)$$

where η_0 is the solvent viscosity and $\epsilon = 1$ since there is no swelling of the unsolvated polymer in this defined reference state; as

$$f_s = 6\pi\eta N_0 \left(\frac{3v\epsilon}{4\pi} \right)^{1/3} \quad (9b)$$

where η and ϵ are, respectively, the viscosity and effective volume factor predicted from eqs. (2) and (6) for equivalent swollen spherical polymers undergoing predominantly hydrodynamic interactions; and as

$$f_T = 6\pi\eta_T N_0 \left(\frac{3v\epsilon_T}{4\pi} \right)^{1/3} \quad (9c)$$

where η_T is the viscosity of swollen, nonspherical, rigid cellulose acetate particles in solution, as measured experimentally. The effective volume factor ϵ_T is the total apparent effective volume factor determined from experimental viscosity measurements and encompassing the effects of swollen, nonspherical, inflexible cellulosic materials experiencing both hydrodynamic and nonhydrodynamic interactions in solution. ϵ_T is determined from experimental viscosity measurements of concentrated solutions by solving eq. (2) to determine the effective volume fraction ϕ_T which would exhibit the observed viscosity η_T . Since $\phi_T = (g_T \epsilon_T) / \rho$ from eq. (3), a total effective volume factor ϵ_T is determinable from the optimized volume fraction and the experimental concentration ($g_T = g_{\text{experimental}}$). Thus, from experimental measurements of concentrated solution viscosities, it is possible to distinguish the relative effects of solvation and asymmetry through an evaluation of f_s and f_T as defined above.

For a given polymer, the absolute magnitudes of the friction coefficients will be strongly dependent on the solvent being examined. But the values of f_s and f_T relative to the unsolvated sphere f_0 will permit a reasonable correlation between different solvents: f_s/f_0 = molar frictional ratio repre-

TABLE I
Mark-Houwink Constants and Effective Volume Factors at Infinite
Dilution for Cellulose Acetate in Various Solvent Systems

Solvent	$K \times 10^4$, dl/g ^a	α^a	ϵ_0	
			$M = 30,270$	$M = 27,350$
Acetone	4.46	0.73	43.75	40.62
Dimethylformamide	17.36	0.62	54.18	50.87
Nitromethane	14.57	0.63	50.41	47.29
1,4-Dioxane	14.37	0.63	49.72	46.64
Methyl formate	4.70	0.72	41.16	38.26
Solvent I	5.11	0.73	48.55	45.09
Solvent II	13.13	0.64	48.83	45.77

^a From ref. 11.

representative of the effect of solvation; f_T/f_s = molar frictional ratio representative of particle nonsphericity; and f_T/f_0 = molar frictional ratio representative of the total effect of shape and solvation on the polymer solution viscosity.

The solvents and mixed solvents studied in this work are summarized in Table I along with their appropriate Mark-Houwink constants and their effective volume factors at infinite dilution. An example of the values of the various parameters determined from eqs. (2) to (9) is presented in Table II for several concentrations of cellulose acetate ($M = 30,270$) in methyl formate. The values of the molar frictional coefficients and the frictional ratios defined above were determined for each solvent system for an experimental range of concentrations up to 20 g/dl (concentrations in g/dl are denoted g'). All solvent systems exhibited the same general variation in frictional ratios with concentration. This behavior is exemplified by cellulose acetate ($M = 30,270$) in acetone at 25°C, as represented in Figure 1. The natural logarithms of the frictional ratios have been plotted to facilitate easy graphic representation of the results. The variance in the logarithms of the frictional ratios for the different solvents at a specified concentration is not large, being on the average less than 3% of the mean value for all solvents at that concentration.

The divergence of f_T/f_0 from f_s/f_0 with concentration can be conveniently represented as a difference in the logarithmic values according to the mathematical relationship

$$\Delta = \ln_e f_T/f_0 - \ln_e f_s/f_0 = \ln_e f_T/f_s. \quad (10a)$$

All relationships were linear (Fig. 2) over the concentration ranges examined, with each solvent exhibiting a different rate of change of Δ with concentration. This variation in slope with concentration (i.e., Δ/g') is necessarily a function of the specific polymer-solvent interactions. The parameter which is most easily and most efficiently characterizes these interactions, as well as explicitly involving the effects of solution temperature and polymer molecular weight, is the effective volume factor at infinite

TABLE II
Characteristic Parameters for Cellulose Acetate^a in Methyl Formate at 25°C

Concn., g/dl	ϵ_T	η , poise	η_T , poise	$f_s \times 10^{-17}$, g/sec·mole	$f_T \times 10^{-17}$, g/sec·mole	η_T/η_s	f_T/f_s	$\frac{f_T/f_s}{\eta_T/\eta_s}$	$(\epsilon_T/\epsilon)^{1/2}$
1.0	26.07	.00694	.00789	.4902	.5793	1.137	1.182	1.040	1.040
2.5	16.76	.0152	.0235	.9291	1.496	1.546	1.610	1.041	1.043
5.0	10.52	.0394	.1014	2.056	5.489	2.574	2.670	1.037	1.037
10.0	6.02	.1434	.9459	6.214	42.04	6.596	6.765	1.026	1.027

^a Polymer: Cellulose acetate, $M = 30,270$; solvent: methyl formate; constants: $K = 4.7 \times 10^{-4}$ dl/g; $\alpha = 0.72$; $\eta_0 = 0.00352$ poise; $f_0 = 0.0838 \times 10^{18}$ g/sec·mole; $\epsilon_0 = 41.16$; $\epsilon_s = 2.60$.

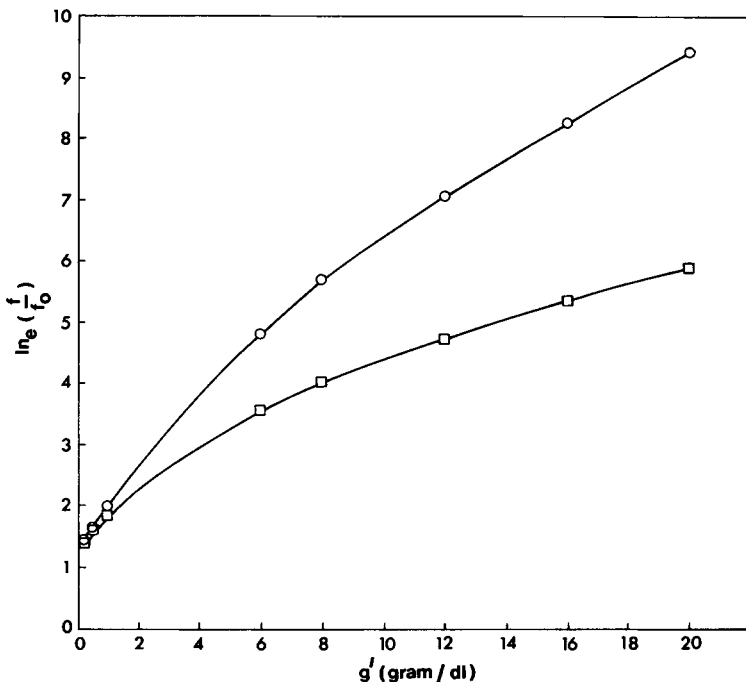


Fig. 1. Variation in frictional ratios with concentration: (○) $\ln_e f_T/f_0$; (◻) $\ln_e f_s/f_0$.

dilution ϵ_0 . The rate of divergence of frictional coefficients with concentration, i.e.,

$$\frac{\ln_e (f_T/f_s)}{g'} = \frac{\Delta}{g'}$$

as a function of the effective volume factor at infinite dilution is plotted in Figure 3. For the polymer-solvent systems studied, a good linear relationship is apparent.

If the main application of the above work is to predict the viscosities of concentrated cellulose acetate solutions, it is perhaps most expedient to not determine the molar frictional coefficients, but rather to deal directly with the appropriate viscometric parameters. In an approach parallel to that used to determine the variation in the logarithms of the frictional ratios f_T/f_s with concentration in Figure 2, the deviation between experimental solution viscosity and that viscosity predicted by the theory of Rudin and Johnston^{6,7} can be evaluated. The plot of the logarithms of the ratio of the appropriate viscosities, i.e., $\ln_e \eta_T/\eta$, as a function of concentration gives similar results to those represented in Figure 2, namely, linear relationships which intercept the origin and exhibit different slopes for the different solvents. In fact, the plots are essentially coincident with the frictional ratio plots for the same solvents, except that the slopes of the

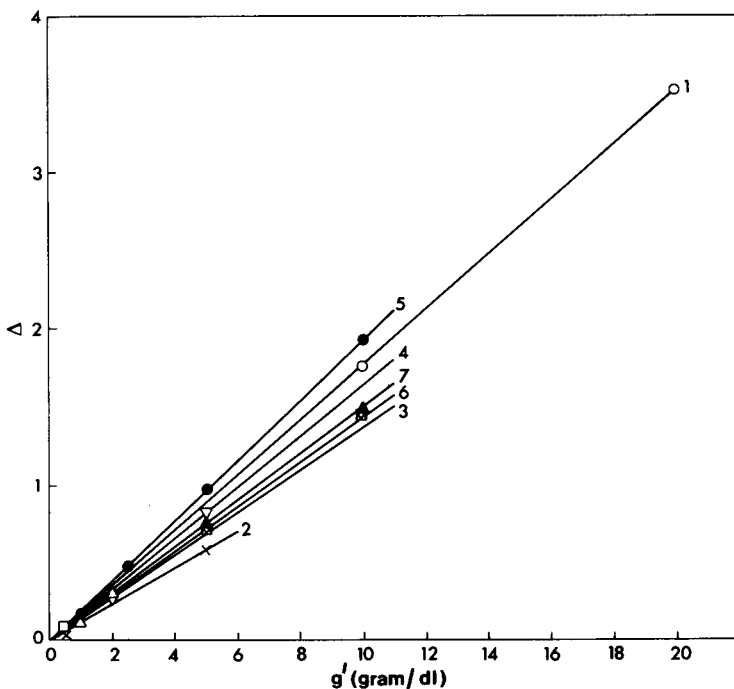


Fig. 2. Variation in frictional ratios $\Delta = \ln_e f_T/f_s$ with concentration for different solvents: (1) acetone; (2) N,N-dimethylformamide; (3) nitromethane; (4) 1,4-dioxane; (5) methyl formate; (6) solvent I; (7) solvent II.

viscosity ratio plots are very slightly lower. This is expected, since the ratio of the molar frictional coefficients can be simplified to the form

$$f_T/f_s = \eta_T/\eta \left[\frac{\epsilon_T}{\epsilon} \right]^{1/3}. \quad (11)$$

Thus, the viscosity ratio η_T/η is less than the corresponding frictional ratio by the factor $(\epsilon_T/\epsilon)^{1/3}$. For the systems examined in this work, the maximum value of $(\epsilon_T/\epsilon)^{1/3}$ (for cellulose acetate $M = 30,270$, in methyl formate at a concentration of 2.5 g/dl) caused the frictional ratio to exceed the viscosity ratio by 4%. Representative values are summarized in Table II. The mean difference between the frictional and viscosity ratios was less than 2% for all the polymer-solvent systems at the various concentrations. Consequently, it is possible to write

$$\Delta = \ln_e(f_T/f_s) = \ln_e(\eta_T/\eta) \quad (10b)$$

as a good approximation.

A computer best fit was performed on the f_T/f_s and η_T/η data that is plotted in Figure 3. Two calculations were performed, one in which all the experimentally obtained points were considered (Case I) and one in which those points (\square^6 , Δ^6 , \circ^4) which deviate notably from the main

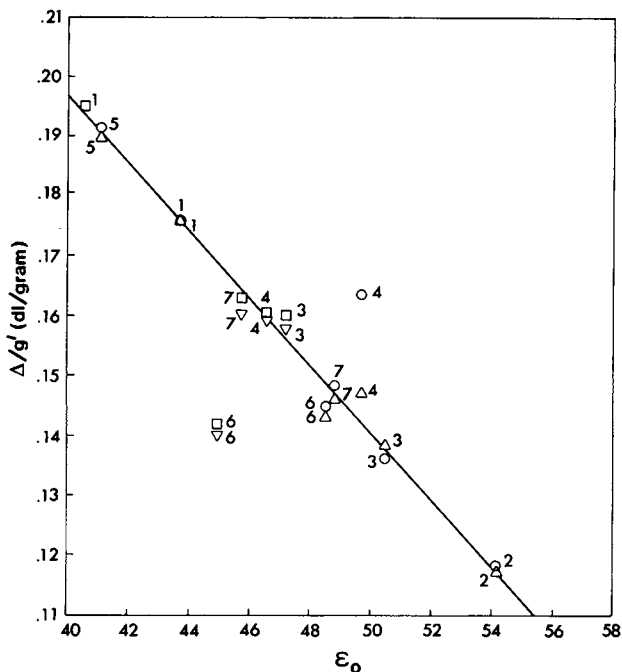


Fig. 3. Variation in rate of change in Δ with concentration as a function of the effective volume factor at infinite dilution (ϵ_0)

$$\begin{array}{ll}
 [\circ] M = 30,270 \} & \Delta = \ln_e f_T/f_s \\
 (\square) M = 27,350 \} & \\
 (\Delta) M = 30,270 \} & \Delta = \ln_e \eta_T/\eta \\
 (\nabla) M = 27,350 \} &
 \end{array}$$

The numerical designations refer to the solvents identified for Fig. 2.

locus of points were not included (Case II). The results are summarized in Table III.

On the basis of these determinations, a single best-fit line was drawn through the locus of points in Figure 3 according to the data set C, case II parameters characterized in Table III. It is felt that this line adequately represents the variation of both the frictional ratios and the viscosity ratios with concentration as a function of the effective volume factors at infinite dilution. Thus, Figure 3 permits accurate estimations of concentrated cellulose acetate solution viscosities as well as the appropriate molar frictional coefficients.

This method of predicting viscometric behavior of concentrated cellulose acetate solutions is both mathematically explicit and easy to apply. The need for a standard reference material such as cotton linters is eliminated by the use of a mathematically defined reference state. Actual viscometric predictions are straightforward, essentially requiring a calculation of the effective volume factor at infinite dilution, ϵ_0 , and the application of this

TABLE III
Correlation of $\ln_e f_T/f_s$ and $\ln_e \eta_T/\eta$ with the Effective Volume
Factors at Infinite Dilution

Data set ^a	Case I			Case II		
	Slope	Intercept at $\epsilon_0 = 40$	Correlation coefficient ^b	Slope	Intercept at $\epsilon_0 = 40$	Correlation coefficient ^b
A	-0.005093	0.1930	-0.8890	-0.005740	0.1979	-0.9956
B	-0.004988	0.1891	-0.9020	-0.005449	0.1968	-0.9896
C	-0.005083	0.1914	-0.8940	-0.005645	0.1968	-0.9929

^a Data set A is for the plot of $\ln_e f_T/f_s$ vs. ϵ_0 ; data set B is for the plot of $\ln_e \eta_T/\eta$ vs. ϵ_0 ; and data set C is the combination of data sets A and B. Each of these data sets includes the experimental results for the cellulose acetates of both 30,270 and 27,350 molecular weights.

^b From ref. 20.

value to Figure 3 to give a specific value of Δ/g' for the solvent system under consideration. The value of Δ ($= \ln_e f_T/f_s = \ln_e \eta_T/\eta$) is then known for any concentration, g' , of cellulose acetate in that solvent. The basic solution theory of Rudin and Johnston^{6,7} permits ready evaluation of f_s and η , thereby enabling accurate estimation of cellulose acetate solution viscosities and related effective molar frictional coefficients.

It should be noted that because of the manner in which the molar frictional coefficients are defined in this work, they may differ slightly from these previously proposed¹² on the basis of shape and solvation. This follows because the f_s value determined here is for spherically swollen polymers experiencing predominantly hydrodynamic interactions, and the f_T value further includes the effects of nonsphericity as well as all interactions other than hydrodynamic interactions that occur in solution. It is the inclusion of these nonhydrodynamic interactions in the f_T term which may give it a magnitude greater than that previously envisioned when only the effect of shape was considered.

Although the final results presented in Figure 3 were obtained using two different molecular weights of the same polymeric material (Eastman cellulose acetate with 39.8% acetylation) at 25°C, the same calibration curve should be adequate for different molecular weight cellulose acetates having similar extents of acetylation over a reasonable range of solution temperatures. It is important to realize that viscometric behavior of cellulose acetates is strongly dependent on the type of cellulose used in making the cellulosic derivative.⁹ Consequently, the validity of Figure 3 should be checked experimentally before using it as a predictive tool for cellulose acetates obtained from notably different sources.

CONCLUSIONS

Concentrated solutions of cellulose acetate are used in a variety of applications, ranging from casting solutions for reverse osmosis membranes to paint formulations. However, because of their tendency to exist in

solution as rigid, extended entities, it has not been possible to predict their solution behavior with any certainty.

The present study has shown that the rapid increase in viscosity with concentration for cellulose acetate solutions is due to the nonsphericity of the polymer molecules as well as the tendency of these molecules to undergo extensive nonhydrodynamic interactions.

Concentrated viscosity effects for cellulose acetate can be predicted by applying the basic solution theory of Rudin and Johnston^{6,7} and extending it through the use of an empirically derived calibration curve (Fig. 3). In this manner, accurate predictions of concentrated solution viscosities as well as molecular asymmetry and the extent of nonhydrodynamic interactions can be calculated for cellulose acetate solutions. The only information required to calculate such behavioral characteristics are the relevant Mark-Houwink constants, solution temperature, polymer molecular weight, and polymer concentration in the solution. As most of this information is readily obtainable, an efficient method to predict cellulose acetate solution behavior is available.

The authors are grateful to H. Huneault for assistance in the progress of these investigations.

References

1. H. K. Johnston and S. Sourirajan, *J. Appl. Polym. Sci.*, **17**, 3717 (1973).
2. W. R. Moore and A. M. Brown, *J. Colloid Sci.*, **14**, 343 (1959).
3. P. J. Flory, O. K. Spurr, Jr., and D. K. Carpenter, *J. Polym. Sci.*, **27**, 231 (1958).
4. W. R. Moore and A. M. Brown, *J. Colloid Sci.*, **14**, 1 (1959).
5. W. R. Moore and G. D. Edge, *J. Polym. Sci.*, **47**, 469 (1960).
6. A. Rudin and H. K. Johnston, *J. Paint Technol.*, **43**, 39 (1971).
7. A. Rudin and H. K. Johnston, *J. Paint Technol.*, **44**, 41 (1972).
8. G. A. Richter and L. E. Herdle, *Ind. Eng. Chem.*, **49**, 1451 (1957).
9. J. K. Watson and D. R. Henderson, *Tappi*, **40**, 686 (1957).
10. F. L. Wells, W. C. Schattner, and S. Walker, Jr., *Tappi*, **46**, 581 (1963).
11. H. K. Johnston and S. Sourirajan, *J. Appl. Polym. Sci.*, **16**, 3375 (1972).
12. B. Jirgensons, *Organic Colloids*, Elsevier, New York, 1958, p. 367.
13. T. F. Ford, *J. Phys. Chem.*, **64**, 1168 (1960).
14. A. Rudin and H. K. Johnston, *J. Polym. Sci.*, **9**, 55 (1971).
15. B. Jirgensons and M. E. Straumanis, *A Short Textbook of Colloid Chemistry*, Pergamon, London, 1954, p. 209.
16. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 2559 (1970).
17. H. K. Johnston and S. Sourirajan, *J. Appl. Polym. Sci.*, **17**, 2485 (1973).
18. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley, New York, 1966, p. IV-79.
19. T. Svedberg and K. O. Pedersen, *Die Ultrazentrifuge*, Th. Steinkopf, Dresden und Leipzig, 1940.
20. F. A. Graybill, *An Introduction to Linear Statistical Models*, Vol. 1, McGraw-Hill, New York, 1961.

Received November 26, 1973

Revised January 25, 1974