

## NOTES

*Mark-Houwink Constants for Some Cellulose Acetate-Organic Solvent Systems*

## INTRODUCTION

Cellulose acetates have a number of industrial applications,<sup>1</sup> and the one which prompted this study is their application for making reverse osmosis membranes.<sup>2</sup> In this process there is a continuing need for expressing the relative solvent power of different solvents, or solvent systems, for cellulose acetate in some quantitative manner.<sup>3,4</sup> The general applicability of the Mark-Houwink equation

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

where  $[\eta]$  is the limiting viscosity number,  $M_v$  is the viscosity-average molecular weight, and  $K$  and  $\alpha$  are empirical constants (Mark-Houwink constants), for many polymer-solvent systems offers a means of expressing solvent powers of different solvents for a given polymer through their relative values of  $K$  and  $\alpha$ . A method is described below for establishing the values of  $K$  and  $\alpha$  for some industrially important cellulose acetates with acetone as the solvent. These values may then serve as a reference to which the corresponding values in other solvents may be compared for the purpose of expressing their relative solvent powers for the given polymer.

## EXPERIMENTAL

Six grades of Eastman cellulose acetates were considered. They are E-398-3, E398-6, E-398-10, E394-30, E-394-45, and E-394-60. The first three grades have acetyl contents of 39.8%, and the remaining grades have acetyl contents of 39.4%. The numbers 3, 6, 10, 30, 45, and 60 included in the Eastman designations refer to increasing viscosity grades represented by the drop times for standard falling-ball viscosity determinations.<sup>1</sup> The solvents used in this work were A.C.S. grade C.P. solvents: acetone, methyl formate, ethyl formate, methyl acetate, 1,4-dioxane, nitromethane, N,N-dimethylformamide, and cyclohexanone.

Viscosity measurements were made in a Cannon-Ubbelohde number 75 dilution viscometer at  $25.0 \pm 0.1^\circ\text{C}$ . Maximum solute concentrations ( $c$ ) used were 1.0 g/dl in acetone and 0.5 g/dl in all other solvents. Dilutions of these 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.

## RESULTS AND DISCUSSION

The specific viscosities,  $\eta_{sp}$ , of the various polymer solutions were determined from the relative values of the viscometrically measured solution and solvent flow times ( $t$  and  $t_0$ , respectively) by means of the relationship

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 = \frac{t}{t_0} - 1 \quad (2)$$

where the values of the solution and solvent viscosities ( $\eta$  and  $\eta_0$ , respectively) are considered proportional to  $t$  and  $t_0$  for dilute solutions. The specific viscosity data corresponding to different concentrations were then plotted in the conventional form  $\eta_{sp}/c$  versus  $c$ . These plots were essentially linear in the lower ranges of the concentrations studied, and they were extrapolated to zero concentration to determine the corresponding limiting viscosity number,  $[\eta]$ , defined as

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (3)$$

The values of  $[\eta]$  so obtained for the different cellulose acetates in the various solvents used are given in Table I.

The system cellulose acetate-acetone has been studied extensively by several workers<sup>5-12</sup> who have determined the values of  $K$  and  $\alpha$ , given in Table II, from experimental measurements of  $[\eta]$  and polymer molecular weight. Even though these literature values of  $K$  and  $\alpha$  for the cellulose acetate-acetone system differ significantly, their usefulness stems from the facts that (i) carefully fractionated samples of the polymer were used in all cases, (ii) eq. (1) was found valid for this system by all workers, and (iii)

TABLE I  
Limiting Viscosity Numbers for Cellulose Acetates in Different Solvents

Solvent	Limiting viscosity number $[\eta]$ , dl/g					
	398-3 <sup>a</sup>	398-6	398-10	394-30	394-45	394-60
Acetone	0.817	0.918	1.163	1.287	1.363	1.485
Methyl formate	0.793	0.912	1.074	1.338	1.406	1.522
Ethyl formate	0.774	0.891	1.031	1.293	1.314	1.403
Methyl acetate	0.884	0.968	1.177	1.407	1.503	1.603
1,4-Dioxane	0.988	1.044	1.249	1.574	1.641	1.759
Nitromethane	0.975	1.055	1.267	1.622	1.644	1.778
N,N-Dimethylformamide	1.043	1.157	1.354	1.659	1.730	1.846
Cyclohexanone	1.050	1.158	1.359	1.645	1.720	1.830

<sup>a</sup> Eastman cellulose acetate grade.

TABLE II  
Literature Values of Mark-Houwink Constants  
for the System Cellulose Acetate-Acetone

Range of molecular weights	Range of $[\eta]$ , dl/g	Degree of substitution	Type of measured mol. wt. <sup>a</sup>	$K \times 10^4$ , dl/g	$\alpha$	Reference
11,000-130,000	0.2-2.8	2.32	$M_n$	0.254	1.0	5
20,000-104,000	0.5-2.5	2.32	$M_{sv}$	0.238	1.0	6
10,000-184,000	0.3-3.1	2.38	$M_n$	0.897	0.9	7
26,000-269,000	0.8-5.1	2.25-2.38	$M_{sv}, M_n$	1.6	0.82	8
31,000-360,000	0.6-3.5	2.38	$M_n$	1.49	0.82 <sup>b</sup>	9
34,000-104,000	0.9-2.3	2.25	$M_n$	2.8	0.78	10
29,000-308,000	0.5-6.0	—	$M_n$	3.51	0.76	11
6,000-105,000	~1-~3	2.32	$M_v$	8.9	0.67	12

<sup>a</sup>  $M_n$  = Number-average molecular weight determined by osmometry;  $M_{sv}$  = molecular weight determined by sedimentation velocity in ultracentrifuge;  $M_v$  = viscosity-average molecular weight.

<sup>b</sup>  $T = 26.5 \pm 0.05^\circ\text{C}$ .

number-average ( $M_n$ ), viscosity-average ( $M_v$ ), and weight-average ( $M_w$ ) molecular weights are identical for a truly monodisperse polymer.

The technique used in this work for determining the relative values of the Mark-Houwink constants for cellulose acetates in different solvents was as follows.

Using the experimental values of  $[\eta]$  for the cellulose acetate-acetone systems obtained in this work (Table I) and each set of the  $K$  and  $\alpha$  values given in the literature for similar systems (Table II), the viscosity-average molecular weight ( $M_v$ ) of each polymer was calculated. Thus a set of eight values of  $M_v$  was obtained for every cellulose acetate sample; the average of these eight values was designated as  $\bar{M}_v$ . The calculated  $M_v$  and  $\bar{M}_v$  are given in Table III. The good correlation of the calculated  $M_v$  values

TABLE III  
Calculated Viscosity-Average Molecular Weights of Cellulose Acetates Used

Literature reference to $K$ and $\alpha$ values used	Molecular weight $M_v$					
	398-3 <sup>a</sup>	398-6	398-10	394-30	394-45	394-60
5	32,170	36,140	45,790	50,670	53,660	58,470
6	34,330	38,570	48,870	54,080	57,140	62,400
7	25,080	28,550	37,130	41,560	44,293	48,720
8	33,270	38,350	51,180	57,910	62,110	68,950
9	36,290	41,830	55,820	63,170	67,740	75,210
10	27,690	32,160	43,550	49,590	53,380	59,580
11	26,920	31,390	42,850	48,960	52,800	59,100
12	26,430	31,460	44,770	52,080	56,740	64,490
	Average molecular weight $\bar{M}_v$					
	30,270	34,810	46,250	52,250	55,980	62,110

<sup>a</sup> Eastman cellulose acetate grade.

despite the use of quite divergent pairs of Mark-Houwink constants suggests that there may be a strong interdependence between  $K$  and  $\alpha$ . Such a possibility has previously been suggested,<sup>13</sup> but, although supported by work in other polymer-solvent systems,<sup>14</sup> no explicit relationship between the two constants has yet been determined. The values of  $\bar{M}_v$  are correlated with the corresponding  $[\eta]$  values in Figure 1, which shows that  $\log_{10} [\eta]$  versus  $\log_{10} \bar{M}_v$  is a good straight line, confirming the applicability of the form of eq. (1) for all the cellulose acetate samples studied.

The independence of the limiting viscosity number of cellulose acetate from the degree of esterification has been found unique to the acetone system.<sup>15</sup> The relevant Mark-Houwink relationship representing the above straight line was found to be

$$[\eta] = 1.56 \times 10^{-4} \bar{M}_v^{0.83} \text{ (dl/g)} \quad (4)$$

which gives the values of  $1.56 \times 10^{-4}$  dl/g for  $K$  and 0.83 for  $\alpha$  for the cellulose acetate-acetone systems.

Rudin et al.<sup>16</sup> have shown that it is possible to predict the weight-average molecular weight of a polymer from a linear extrapolation of  $M_v$  versus  $\alpha$  to  $\alpha = 1$ . For samples of polydisperse polystyrene (PS) and poly(methyl methacrylate) (PMMA) in various solvents, the values of  $M_w$  so estimated were within 10% of the experimentally determined values. In the literature,<sup>19,20</sup> an  $\alpha$  value of 0.8 or higher is associated with good solvent power and high solution stability of polymer-solvent systems. Hence values of  $M_v$  at  $\alpha = 0.83$  may be expected to approximate  $M_w$  reasonably well. This is confirmed

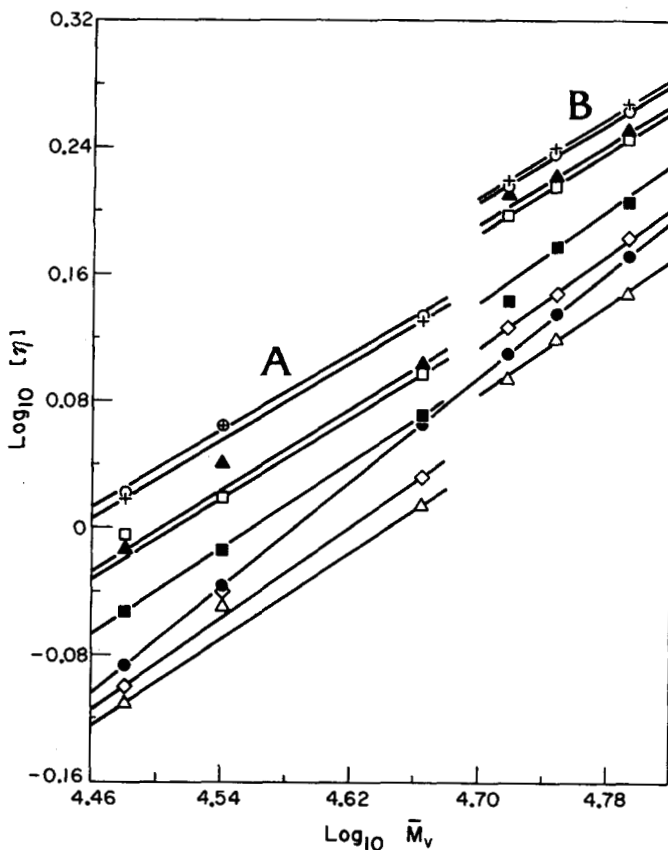


Fig. 1. Mark-Houwink relationship for cellulose acetate-organic solvent systems: acetyl content of cellulose acetate: A, 39.8%; B, 39.4%. Solvents: (●) acetone; (◇) methyl formate; (△) ethyl formate; (■) methyl acetate; (□) 1,4-dioxane; (▲) nitromethane; (○) cyclohexanone; (+) N,N-dimethylformamide.

by a comparison of the experimentally determined molecular weights of PS and PMMA with those estimated from the extrapolation of  $M_w$  versus  $\alpha$  to  $\alpha = 1$  (technique of Rudin et al.<sup>18</sup>) and to  $\alpha = 0.83$ . These results, given in Table IV, show that in nine out of ten cases studied, the estimated values of  $M_w$  have the same order of precision when compared to the experimental values. Consequently, it seems justifiable that the values of  $M_w$  used in obtaining eq. (4) can be considered to approximate an effective  $M_w$  (which is independent of solvent system) for the practical purpose of comparing the relative solvent power of different solvents for cellulose acetate.

On the basis of the foregoing considerations, the experimental values of  $[\eta]$  obtained for cellulose acetates in the other solvents were correlated with the same values of  $\bar{M}_v$  as those used for acetone. These correlations, given in Figure 1, showed that the form of eq. (1) was reasonably valid for all the systems studied, and the Mark-Houwink constants were functions of both the chemical nature of the solvent and the acetyl content of cellulose acetate.

Employing the above techniques for most polymer-solvent systems should be straightforward, but care must be taken that the molecular weight distributions of the calibration and unknown polymers are similar or the derived relations may not be applicable.

TABLE IV  
Comparison of Experimental and Estimated Weight-Average Molecular Weights of Polystyrenes (PS) and Poly(methyl Methacrylates) (PMMA)

Polymer <sup>a</sup>	Experimental <sup>a</sup>	Molecular weight $M_w$			
		Estimated		Estimated	
		For $\alpha = 1^a$	Error, % <sup>b</sup>	For $\alpha = 0.83$	Error, % <sup>b</sup>
PS-K1	240,900	250,600	4.0	216,500	-10.1
PS-K2	280,600	254,500	-9.3	242,900	-13.4
PS-D8	315,900	295,700	-6.4	279,300	-11.6
PS-K3	335,000	396,000	18.2	326,100	-2.7
PMMA I <sup>c</sup>	1,790,000	1,570,000	-12.3	1,160,000	-35.2
PMMA II <sup>c</sup>	3,250,000	3,710,000	14.2	3,070,000	-5.5
PS I <sup>c</sup>	1,250,000	1,450,000	16.0	1,100,000	-12.0
PS II <sup>c</sup>	239,000	250,000	4.6	234,000	-2.1
PS <sup>d</sup>	1,550,000	1,635,000	5.5	1,550,000	0
PS <sup>d</sup>	1,550,000	1,648,000	6.3	1,550,000	0

<sup>a</sup> Polymer nomenclature and data on experimental and estimated molecular weights are as given by Rudin et al.<sup>16</sup>

$$^b \text{Error} = \frac{M_{\text{estimated}} - M_{\text{exptl.}}}{M_{\text{exptl.}}} \times 100.$$

<sup>c</sup> Data of Lundberg, Hellman, and Frisch.<sup>17</sup>

<sup>d</sup> Data of Oth and Desreux.<sup>18</sup>

The false viscosity effect<sup>21-24</sup> of cellulose acetate should exert no influence on the determined Mark-Houwink constants in the various solvents<sup>25</sup> since those constants are determined by extrapolation to infinite dilution.

The values of  $K$  and  $\alpha$  obtained for the different cellulose acetate-organic solvent systems studied are given in Table V. It is suggested that the values of Mark-Houwink constants obtained by the foregoing method together give a quantitative measure of the relative solvent power of different solvents (or solvent systems) for cellulose acetates, and the above constants can be used to calculate the coagulation half-life for the polymer

TABLE V  
Mark-Houwink Constants for Cellulose Acetate-Organic Solvent Systems

Solvent	Acetyl content of cellulose acetate			
	39.8%		39.4%	
	$K \times 10^4$ , dl/g	$\alpha$	$K \times 10^4$ , dl/g	$\alpha$
Acetone	1.56	0.83	1.56	0.83
Methyl formate	4.70	0.72	4.00	0.74
Ethyl formate	6.94	0.68	5.57	0.71
Methyl acetate	8.80	0.67	9.84	0.67
1,4-Dioxane	14.37	0.63	15.05	0.64
Nitromethane	14.57	0.63	16.99	0.63
N,N-Dimethylformamide	17.36	0.62	19.71	0.62
Cyclohexanone	19.54	0.61	21.80	0.61

in different solvent systems.<sup>20,26</sup> A scale of solvent power of different solvent systems relative to the values of  $K$  and  $\alpha$  obtained for acetone in this work may find useful application in the development of cellulose-acetate reverse osmosis membranes.

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