On the Structure of Concentrated Cellulose Acetate Solutions*

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Synopsis

The supermolecular structure of cellulose acetate membrane casting solutions was determined by measuring their rheological behavior. The method was applied to both clear and turbid casting solutions. The resulting data on activation energy of viscous flow are shown to depend on the cellulose acetate content of the casting solution and on the nature of solvent used. The separation properties of the prepared asymmetric membranes determined by reverse osmosis testing indicate a good correlation with the data obtained by the rheological measurements of the casting solutions. The latter can, therefore, be used as a practical tool for the investigation of early stages in the asymmetric membrane formation process.

INTRODUCTION

Since Loeb and Sourirajan[1] first prepared asymmetric cellulose acetate membranes, much work has been done to elucidate their formation mechanism. A number of proposed concepts dealing with this problem have been reviewed elsewhere.[2,3] All the approaches used were based on the phenomenon of phase separation within a cast solution layer as the crucial step during membrane formation.

The solution structure–evaporation rate concept for controlling the porosity of asymmetric cellulose acetate membranes[4–10] has particularly emphasized two parameters affecting the phase change within the solution layer: the rate of solvent removal from the solution surface and the structure of casting dope, i.e., the state of polymer supermolecular aggregation in it. Whereas the first parameter has been successfully measured,[5] the second could not be easily defined. Indirect conclusions concerning its relative value were made,[5] and only recently[2] a direct, light-scattering technique was applied to indicate the extent of polymer supermolecular ordering in the membrane-casting solutions. A correlation of the data obtained by such measurements with the properties of prepared asymmetric membranes has shed more light on the early stage of membrane formation and contributed to more controllable membrane preparation.

A main drawback of the light-scattering characterization method is its inapplicability to turbid solutions which are very often used for asymmetric membrane making. Such typical turbid membrane-casting solutions are, for example,

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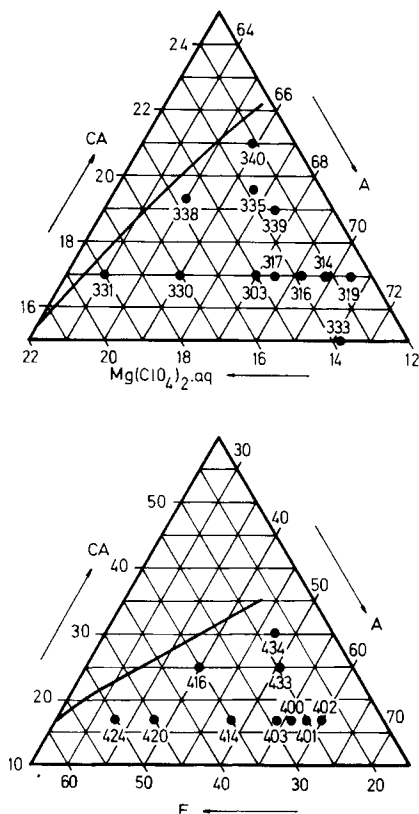
Fig. 1. Compositions of membrane casting solutions and corresponding phase separation boundaries.

Loeb-Sourirajan-type mixtures consisting of cellulose acetate, acetone, and aqueous magnesium perchlorate. The objective of this paper is, therefore, to characterize various cellulose acetate membrane casting solutions by measuring their rheological properties, viz., to use a method which is applicable to turbid solutions as well.

The viscosity coefficient of concentrated polymer solutions is known to depend on the applied shear stress. The flow of such solutions at low shear stresses is Newtonian, which means that the solution viscosity coefficient at such conditions is constant. Low shear stresses applied to the concentrated polymer solution cannot break down the strutures present in it; hence, the Newtonian viscosity measured at low shear stresses describes the solution flow without any disturbance of its structure. The viscosity measurements can thus be used[11,12] for characterizing the state of supermolecular polymer ordering in a concentrated polymer solution.

It was also found[13] more appropriate to employ the temperature dependence of solution viscosity rather than the viscosity itself, as a value related to the polymer solution structure. The temperature dependence of viscosity has been theoretically derived by Eyring[14] who treated the flow as an activation process, and the temperature–viscosity relationship was given in the form

$$\eta = A e^{E_{\mathrm{visc}}/RT}$$

where E_{visc} = energy of activation of viscous flow. This quantity depends on the same parameters as the viscosity coefficient η, i.e., on polymer concentration, temperature, and nature of solvent, and it was used here to characterize quantitatively the state of structurization of the membrane casting solutions.

The applicability of the rheological testing method was checked with various membrane casting solutions, and the results obtained were correlated to characteristic properties of the membranes made from all the employed casting solutions. Properties which supply information on average pore size on the membrane surface are the separation of solute (sodium chloride) of thermally untreated membrane and/or the membrane shrinkage temperature profile giving the temperature needed for a membrane to achieve a certain level of solute separation.

EXPERIMENTAL

Materials and Solutions

Eastman cellulose acetate E-398-3 and reagent-grade acetone, formamide, and magnesium perchlorate were employed for both the solution preparation for viscosity measurements and the membrane casting.

Two series of solutions, the first using aqueous magnesium perchlorate with magnesium perchlorate–water ratio of 1:8.5 (series 300) and the second using formamide (series 400) as the swelling agents, were prepared (Table I.). The positions of points representing the casting solution compositions in relation to the phase separation boundaries for the two systems are shown in triangular polymer–solvent–swelling agent diagrams in Figure 1.

Determination of Solution Viscosity

The viscosity of concentrated polymer solutions is usually measured by rotational viscometers. These are rather sophisticated and expensive devices and it did not seem appropriate to use them in the exploratory experiments, the more so because some practical problems with the membrane casting solutions became evident. One of them related to the casting solution composition, which usually contains a low-boiling liquid (acetone) as solvent component. Viscosity measurements should, therefore be carried out in a closed system.

The simplest approach at present was to use a rolling ball type instrument such as a Hoeppler viscometer, in which the shear stress value depends on the density difference between the ball and the investigated solution. Low shear stresses which keep the flow of a concentrated casting solution within the Newtonian region can be achieved by using a glass ball of relatively low density. Klein[12] has pointed out that the temperature dependence of the viscosity can be determined satisfactorily in the Hoeppler viscometer if the same ball is used throughout the measurements. In such a way, all the measurements are performed at constant, low shear stress, a condition rendering comparable viscosity values. Even a slight deviation from the Newtonian type of flow is allowed without any noticeable error in the finally calculated E values.

The determination of the solution viscosity in the Hoeppler viscometer con-

sisted in measuring the rolling time of a ball between two marks in the viscometer tube. To evaluate the viscosity of a fluid, a simplified equation of the form

$$\eta = k(\rho_s - \rho_-)\theta$$

was applied, where k = the instrument constant obtained by the viscometer calibration with a liquid of known viscosity and density, ρ_s and ρ = densities of the rolling ball and the fluid, respectively; and θ = time of roll. This equation shows that, besides the rolling times at different temperatures, the solution density ρ or, more precisely, its temperature dependence should be determined. A weight dilatometer of the type described by Gibson and Loeffler,[15] used as a pycnometer, was found suitable. The dilatometer partly filled with a known amount of the solution and partly with mercury contained, at various temperatures, different quantities of mercury. The volume changes of the casting solution in the dilatometer were easily calculated from the amount of mercury, its densities at various temperatures, and the volume changes of the dilatometer. Using these data, the absolute value of the solution density at any temperature could be determined.

Membrane Preparation and Testing

Porous asymmetric membranes were cast from all the solutions listed in Table I. Temperature of the casting solutions for the formamide-based membranes was 25°C, and for the series 300 membranes, 0–2°C. The glass plates were kept at the same temperatures as the casting solutions. Temperature of the casting atmosphere was always 20–25°C, and its relative humidity was 65%. The casting was done practically without an evaporation period, i.e., the cast solution was immediately immersed into a gelation bath consisting of ice-cold water. In such a way, the variations in the membrane surface porosities could be attributed to the solution structure effects only, with changes caused by the evaporation step being negligible.

The membranes obtained by the casting procedure were tested in the standard reverse osmosis setup.[16] Reverse osmosis experiments for the membranes in the as-cast condition were carried out at 7.0 atm using a feed solution containing 200 ppm sodium chloride. The thermally treated membranes were tested at 17.4 atm using the 3500-ppm sodium chloride feed solution. Before the reverse osmosis experiment, each film was subjected to a pure-water pressure treatment for 1–2 hr at 20% higher pressure than that to be used in the reverse osmosis run. All experiments were of the short-run type and performed at laboratory temperature. A feed flow rate of 450 cc/min was used, giving a mass transfer coefficient $k = 45 \times 10^{-4}$ cm/sec on the high-pressure side of the membrane.

For all salt concentrations, a conductivity bridge was used for analysis. The fraction solute separation f was calculated from the relation

$$f = \frac{\text{solute concn. in feed (ppm)} - \text{solute concn. in product (ppm)}}{\text{solute concn. in feed (ppm)}}$$

RESULTS AND DISCUSSION

The results of rheological measurements, either in the form of viscosities or as the activation energies of viscous flow, depend on the applied shear stress, the

structure of the polymer chain (its molecular mass, flexibility, etc.), the nature of the solvent, the polymer concentration, and the temperature. As the shear stress in this work was kept at a constant low value, and as the same polymer sample was used throughout the measurements, only the last three variables mentioned were operative.

The form of the log η–$1/T$ relationships presented in Figure 2 for all the cellulose acetate solutions is fairly linear. There is a very slight tendency of some of the highest viscosity values to deviate from linearity, but this can hardly be considered as systematic. The linearity of the log η–$1/T$ relationship is shown[11,12] to be typical of nonassociable fluids or fluids with unchangeable supermolecular associations. Accordingly, the results obtained here indicate that the extent of supermolecular polymer structurization in the cellulose acetate multicomponent solutions practically does not change within the investigated temperature interval. Such a conclusion is not quite in accordance with the behavior of some binary concentrated polymer solutions,[11,12] which exhibit slightly curved log η–$1/T$ dependences, pointing to some changes in the structural properties of the solutions with temperature variation. The explanation of this difference cannot be given yet, because too little is known about the interactions of components

TABLE I
Casting Solution Compositions and Their Activation Energies of Viscous Flow

| Solution type | Solution composition[a] | | | E_{exp}, cal/mole | E_{solv}, cal/mole | ΔE, cal/mole |
	CA, wt-%	Swelling agent, wt-%	SwA/S			
316	17.0	13.8	0.199	9,190	2,580	6,610
339	19.0	13.5	0.200	9,780	2,580	7,200
340	21.0	13.1	0.199	10,380	2,580	7,800
333	15.0	13.8	0.194	8,470	2,530	5,940
316	17.0	13.8	0.199	9,190	2,580	6,610
335	19.6	13.8	0.207	10,000	2,650	7,350
319	17.0	12.5	0.177	9,110	2,280	6,830
314	17.0	13.2	0.189	9,260	2,480	6,780
316	17.0	13.8	0.199	9,190	2,580	6,610
317	17.0	14.5	0.212	9,450	2,690	6,760
303	17.0	15.0	0.221	9,550	2,740	6,810
330	17.0	17.0	0.258	9,710	2,930	6,780
331	17.0	19.0	0.297	10,190	3,080	7,110
335	19.6	13.8	0.207	10,000	2,650	7,350
338	19.3	15.7	0.242	10,260	2,850	7,410
400	17.0	27.0	0.482	8,590	2,230	6,360
433	25.0	24.4	0.482	10,030	2,230	7,800
434	30.0	22.8	0.483	14,220	2,230	11,990
402	17.0	23.0	0.383	8,570	2,110	6,460
401	17.0	25.0	0.431	8,540	2,170	6,370
400	17.0	27.0	0.482	8,590	2,230	6,360
403	17.0	29.0	0.537	8,820	2,290	6,530
414	17.0	35.0	0.729	9,020	2,520	6,500
420	17.0	45.0	1.184	9,760	3,050	6,710
424	17.0	50.0	1.515	10,510	3,440	7,070
433	25.0	24.4	0.482	10,030	2,230	7,800
416	25.0	35.0	0.875	10,960	2,680	8,280

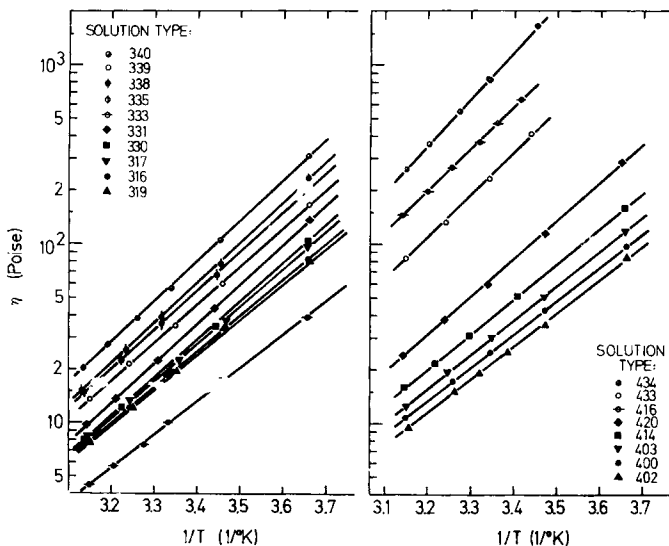[a] CA = cellulose acetate; SwA = swelling agent; S = solvent-acetone

Fig. 2. Plot of log η vs $1/T$ of the membrane casting solutions.

in the process of supermolecular association of both binary and multicomponent concentrated polymer solutions.

The slopes of the log η–$1/T$ dependences for various cellulose acetate solutions differ from each other, which is best expressed by the values of the activation energy of viscous flow, E_{visc}. These are calculated from the experimental data by a least-squares analysis and tabulated in Table I (column 5) along with the compositions of the various casting solutions.

The absolute values of E_{visc} show similar trends for both the aqueous magnesium perchlorate-based and the formamide-based casting solutions (series 300 and 400, respectively). The differences appearing in the activation energies of viscous flow for the various solutions within each of the series are due to the compositional effects, more specifically to changes in the cellulose acetate concentration, and partly to the variation of the solvent nature produced by varying the solvent and swelling agent contents.

An increase in the cellulose acetate content of the casting solution systematically increases its activation energy of viscous flow. Such a trend is most correctly shown in the series of solutions with the same, constant swelling agent-to-solvent ratio, and differing only in the cellulose acetate concentrations (solutions 316, 339, and 340; and 400, 433, and 434, respectively). These results indicate the progressive enlargement of supermolecular structures caused by the increasing cellulose acetate concentration, and they are consistant with both theoretical considerations and the earlier experimental findings.[17]

The nature of the solvent appears to be the second factor which affects the structure of membrane casting solutions and their rheological behavior. Most of the results presented here in the form of E_{visc} values are lower than those reported for the corresponding binary cellulose acetate–dimethylformamide and cellulose acetate–dioxane solutions[11] amounting to 11,000–19,000 cal/mole. This indicates that the solvent power of the acetone–formamide and acetone–aqueous magnesium perchlorate combinations for the secondary cellulose acetate is su-
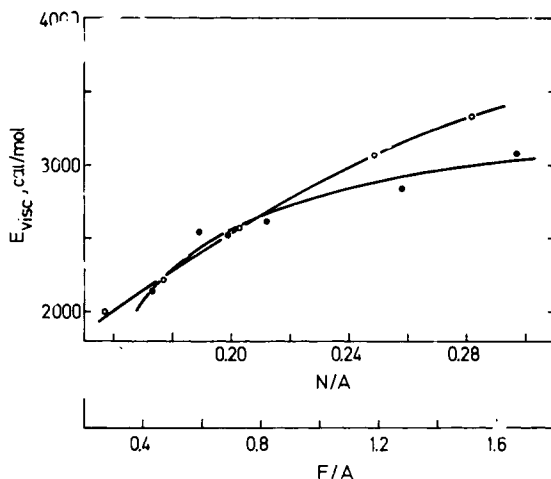
Fig. 3. Activation energies of viscous flow in relation to swelling agent-to-solvent ratio: N = magnesium perchlorate:water = 1:8.5; F = formamide; A = acetone.

perior to that of dimethylformamide and dioxane, i.e., the former mixed solvents produce less structurized cellulose acetate solutions.

The activation energies of viscous flow for the membrane casting solutions of constant (17%) cellulose acetate content consistently rise with increase in swelling agent concentration.   This result would imply an ordering action of the swelling agent on the cellulose acetate solutions in acetone.   In analyzing such data, one must not overlook a variation of the activation energy of flow of the solvent combination itself (solvent + swelling agent) with composition.   The measured E_{visc} values of the solvent composition also happen to rise with an increase of the swelling agent-to-solvent ratio (Fig. 3).   In order to get the real effect of the swelling agent content on the casting solution structure, the E_{visc} values of different cellulose acetate solutions should be corrected by subtracting the activation energies of flow of the corresponding solvent combinations.   By such a procedure, ΔE_{visc} values have been obtained for all the casting solutions (last column in Table I).

Whereas the discussed effect of the cellulose acetate concentration on the corrected activation energies of viscous flow remains the same, the solvent nature dependence changes its character.   This is illustrated in Figure 4, where two sets of data (E_{visc} and ΔE_{visc}) for both series of solutions are plotted against the swelling agent concentration.   In contrast with the steady increase of the activation energies of flow, the ΔE_{visc} values remain practically constant over a fairly wide range of swelling agent content, indicating practically unchanged supermolecular structurization of the cellulose acetate solutions.   This important conclusion is very close to earlier findings,[2] which showed that an increase in the swelling agent concentration may even slightly reduce the casting solution structurization.   Small differences between these two results might be assigned to the different experimental techniques used, which still need improvement in sensitivity.

A massive increase in swelling agent concentration brings the casting solution composition very close to the phase separation boundary [solutions 331 and 424
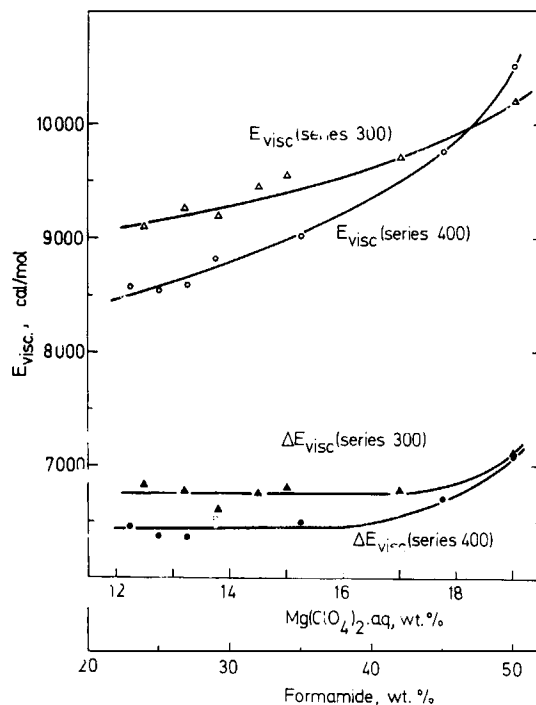
Fig. 4. Activation energies of flow and their corrected values for different membrane casting solutions.

in Fig. 1(a) and (b), respectively] and produces a definite rise in their ΔE_{visc} values, viz., better ordering of polymer structures in the solutions. This observation is consistent with the earlier one,[2] attributed to a modified role of the swelling agents close to phase separation conditions, where they act more as nonsolvents.

TABLE II
Reverse Osmosis Separation of Some Thermally Untreated Membranes

Membrane type	CA in casting solution, wt-%	Sodium chloride separation f
316	17.0	0.348
339	19.0	0.513
340	21.0	0.495
400	17.0	0.272
433	25.0	0.386
434	30.0	0.455

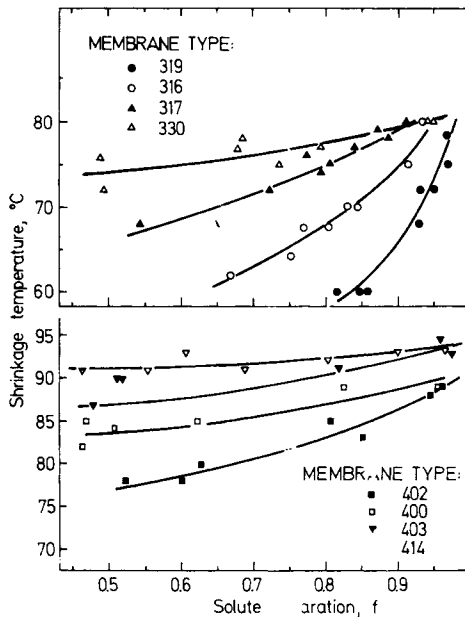| Membrane type	Swelling agent in casting solution, wt-%	Sodium chloride separation f
316	13.8	0.348
303	15.0	0.325
330	17.0	0.250
331	19.0	0.209
402	23.0	0.332
400	27.0	0.272
420	45.0	0.215

Fig. 5. Shrinkage temperature profiles of membranes prepared from some casting solutions.

All structural differences in the membrane casting solutions should be reflected in the properties of prepared asymmetric membranes. According to the improved concept of asymmetric membrane formation,[2] the phase separation process in concentrated cellulose acetate solutions takes place within a long-range dynamic polymer network. The dimensions and density of the polymer structures in a casting solution affect the size and number of droplets of the newly formed phase in the solution's upper layer, and eventually the porosity of the membrane's surface layer. The latter property may be indirectly determined from the reverse osmosis data (sodium chloride separation) of thermally untreated membranes[10] or from the relative positions of membrane shrinkage temperature profiles[5,6] obtained by the usual reverse osmosis experiment. Both types of results give a relative measure of average pore size on the membrane surface in the as-cast condition.

Table II illustrates the effect of changes in the membrane casting solution composition on the average pore size of thermally untreated membranes. An increase of the cellulose acetate content in both series of casting solutions (upper part of Table II) decreases the relative dimensions of average membrane surface pores, which is manifested in higher sodium chloride separation values. The effect is not quite equal for both series of the membrane casting solutions, presumably because of the inherent differences in their nature. When correlated to the results of the supermolecular ordering in the casting solutions obtained rheologically, these data show that more extensive structurization in a casting solution leads to membranes having smaller average pores in the surface region.

A change in solvent nature brought about by an increase in swelling agent content (lower part of Table II) produces membranes with lower separation characteristics, indicating the presence of bigger average pores in the membrane surface. The identical conclusion is obtained from the relative positions of the

membrane shrinkage temperature profiles (Fig. 5). A shrinkage temperature-versus-solute separation curve located at higher temperature points to the presence of relatively big pores on the membranes surface in the as-cast condition, and membranes with smaller pores should be shrunk at lower temperatures to give the same level of solute separation. For instance, the average surface pores in membranes 319 and 402, made from solutions with low swelling agent content, are relatively small, and quite large in membranes 330 and 414. A higher concentration of swelling agent in the cast dope, making the supermolecular network in it looser and less extensive, increases, therefore, the average pore dimensions in the finally prepared membrane.

In conclusion, the results presented here point again to the usefulness of the membrane casting solution structure determination and show that the rheological measurements can be successfully applied for such purposes. They also confirm the validity of the refined membrane formation concept, which takes into account the structure of membrane casting solution and its influence on the events occurring later in the process.

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