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# PHASE SEPARATION PHENOMENA IN SOLUTIONS OF CELLULOSE ACETATE. I. DIFFERENTIAL SCANNING CALORIMETRY OF CELLULOSE ACETATE IN MIXTURES OF DIOXANE AND WATER

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## SYNOPSIS

The nature and kinetics of phase separation processes of solutions of cellulose acetate (degree of substitution, 2.5) in mixtures of dioxane and water are studied by differential scanning calorimetry (DSC). The thermograms on heating show small endothermic effects, detectable only after prolonged aging below the phase separation temperature. Experiments in two regions of the ternary diagram are of interest for the description of the formation mechanism of asymmetric membranes viz., (1) at high polymer and high concentrations and low concentrations of nonsolvent (gelation); (2) at lower polymer concentrations of nonsolvent (liquid-liquid separation followed by gelation). Endothermic effects after prolonged aging are found at high polymer concentrations ( $\geq 40\%$ ). These results demonstrate that gelation is very slow in these systems. At lower concentrations of polymer and high concentrations of nonsolvent (up to 40%) a more rapid type of phase separation can be observed visually on cooling. The temperature where turbidity sets in (the cloud point) is independent of the rate of cooling. In DSC experiments no exothermic effect is found on cooling. Again, after aging an endothermic effect is present. The endothermic peak, which is situated below the cloud point, is probably a result of melting of the gelled concentrated phase.

## INTRODUCTION

In our laboratory we study phase separation processes as a tool for understanding the formation mechanism of hyperfiltration (reverse osmosis) membranes. These membranes have an asymmetric structure. They consist of a thin selective top layer, with a thickness of about 0.2–0.5  $\mu\text{m}$ , on a porous supporting layer, which is about 100  $\mu\text{m}$  thick.

Usually asymmetric membranes of cellulose acetate and other polymers are prepared by casting a concentrated polymer solution (10–30% polymer) as a thin film on a glass plate and immersing this film in a nonsolvent bath. In the film a complicated phase separation process takes place, which is initiated by the exchange of solvent and nonsolvent. These processes are distinctly different for the top layer (the skin) and for the lower layers of the film. The result is a membrane with the above-mentioned asymmetric structure.

Several authors have tried to explain the formation of an asymmetric membrane. Most of the mechanisms proposed are based on thermodynamic considerations of a polymer in a mixed solvent [1-7]. Detailed data, however, are missing on thermodynamics and kinetics of phase separation in concentrated polymer solutions from which membranes are prepared, e.g., cellulose acetate (CA).

In this article we study a number of aspects of phase separation in solutions of CA to which nonsolvent has been added. We will keep circumstances during phase separation constant; hence, exchange processes with a coagulation bath, as in actual membrane formation, are not considered. Differential scanning calorimetry (DSC), as a technique, offers excellent possibilities for the study of phase separation phenomena [8,9]. With this technique we try to gain insight into the demixing process of CA (degree of substitution, 2.5) in mixtures of dioxane and water. The choice of this system is based on the frequent use of dioxane as a solvent in casting solutions [10-14].

## EXPERIMENTAL

### Materials

The CA is from Eastman, catalog number 4644, with acetyl content of 39.8%. Using gel permeation chromatography (GPC) its molecular weight has been characterized as  $\overline{M}_n = 24,000$ ,  $\overline{M}_w = 55,000$ , and  $\overline{M}_z = 118,000$ . Dioxane is 1,4-dioxane of Baker analyzed reagent grade. The water used is distilled twice.

### Cloud Point Measurements

Cloud points were determined in well-homogenized solutions. These mixtures were prepared according to the method of Van Emmerik and Smolders [8]. The desired amounts were weighed in small Pyrex glass tubes. These were degassed and sealed under vacuum at liquid nitrogen temperature. The tubes were heated at 90°C for at least 2 days to obtain homogeneous solutions.

Phase separation (cloud) points were determined by heating or cooling the thermostat bath at a rate of 1°C/h, at 1°C/10 min or at 1°C/3 min.

### Differential Scanning Calorimetry

The solutions were made by weighing the appropriate amounts in sample pans of aluminum or stainless steel. These pans were hermetically sealed. Only sample pans that showed no weight loss after 2 days at 100°C were used. The use of stainless-steel pans is favorable because of the larger quantities that this type of pan can contain. The DSC apparatus used was Perkin-Elmer model DSC 2, equipped with provisions for working below room temperature and with an automatic baseline corrector.

## RESULTS

### Cloud Points

A series of homogeneous CA solutions (weight fractions 0–25%), with constant but different ratios of dioxane to water was chosen. When a homogeneous solution is cooled, a visual perceptible cloudiness appears at a certain temperature. The cloud point curves obtained in this manner are given in Figure 1. The appearance of the cloudiness is not dependent on the rate of cooling within the accuracy of the observations (about 1°C). When we heat the phase-separated solutions from a temperature not far below the cloud point, say 5°C below it, the cloudiness disappears at the temperature where it appeared during the cooling stage. When a demixed solution is centrifuged we obtain a clear dilute phase on top of a cloudy gel-like concentrated phase. We note that this is also the result of aging of a solution at a temperature far below the cloud point temperature. In Figure 2, cloud points have been plotted in a ternary diagram for three temperatures, viz., 20, 30, and 60°C. We note a dramatic influence of the water content on the cloud point temperature. The above given results indicate a process of liquid–liquid phase separation for the region of low polymer concentrations (up to 25%) and fairly high nonsolvent concentrations (up to 40% of the solvent mixture).

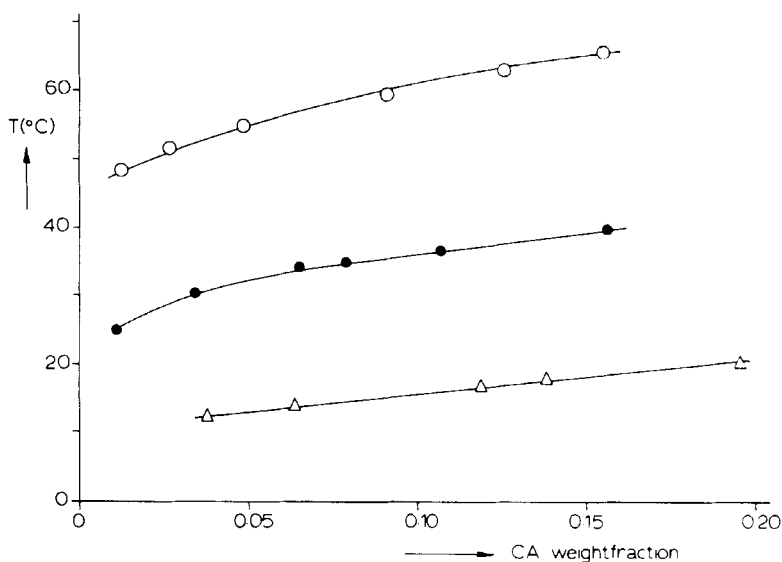


FIG. 1. Cloud point curves in the CA/dioxane/water system: (O) dioxane = 60%, water = 40%; (●) dioxane = 65%, water = 35%; (Δ) dioxane = 70%, water = 30%.

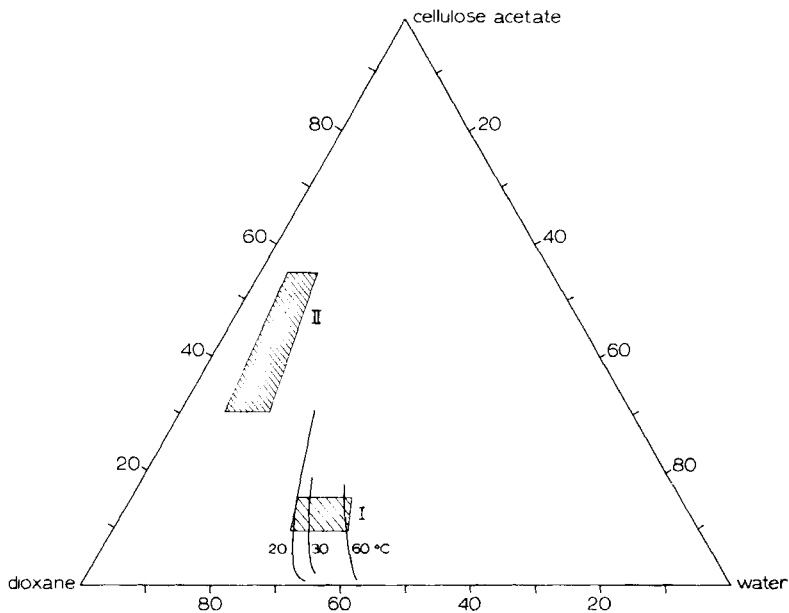


FIG. 2. Ternary diagram for CA/dioxane/water at 20, 30, and 60°C. Special DSC experiments have been carried out in regions I and II.

### Differential Scanning Calorimetry for Solutions within the Two-Phase Region

The area to the right of the curves in Figure 3 is the area with visual phase separation, i.e., we observe a cloudiness upon cooling solutions having compositions in this region of the diagram. We have done a few DSC experiments for solutions containing 9–15% polymer in a mixture of 60% dioxane and 40% water (indicated by the region I in Fig. 2).

Upon cooling these solutions no exothermic heat effect could be observed.

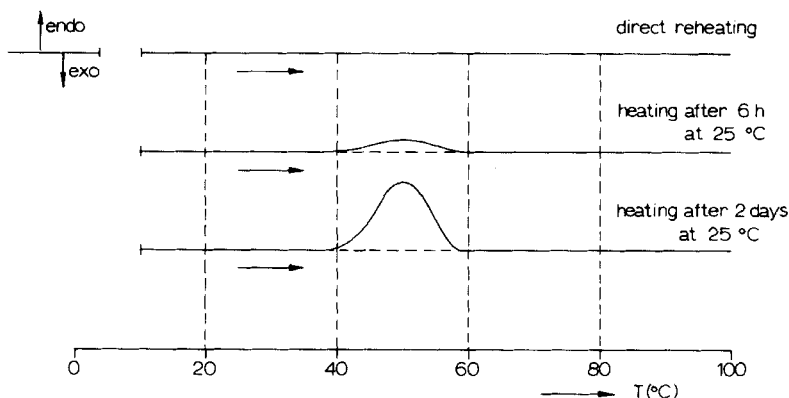


FIG. 3. Endothermic heat effects for a 10% CA solution in a mixture of 60% dioxane and 40% water. Heating after aging at 25°C. The cloud point for this system is 61°C (see Fig. 1).

The temperature range is from 100 to 10°C. The cooling rate was varied between 0.3 and 40°C/min.

Endothermic effects upon reheating have been found only after prolonged aging at temperatures below the phase separation temperature. Some results are given in Figure 3. The samples were aged at 25°C and initially cooled to 10°C. Then the samples were heated at a rate of 10°C/min and the heat effect was recorded.

We note that the magnitude of the heat effect is dependent on the aging time at 25°C and that the place of the peak is independent of the aging time. It is important to note that the peak occurs below the cloud point temperature, which is about 61°C.

### Differential Scanning Calorimetry for Solutions Outside the Two-Phase Area

A number of experiments have been performed in the area of high polymer concentrations and low water content; this is region II in Figure 2. Visually these solutions being 40–50% in polymer concentration are clear at higher temperatures, say above 90°C, at water concentrations of up to 20%.

Below 30% polymer concentration we could not detect endothermic effects in the DSC heating curves in the range from -10 to +100°C, after 2 days of aging time at 25°C. At 40% polymer concentration an endothermic effect upon heating could be determined for mixtures containing 15 and 20% water, respectively, in the solvent mixture. No endothermic effect appears in the thermogram at the ratio 90% dioxane/10% water after 2 days of aging at 25°C (Fig. 4). The heating rate is 10°C/min from 10 to 100°C. In these experiments an exothermic effect could not be found during cooling with variable cooling rates (0.31–40°C/min).

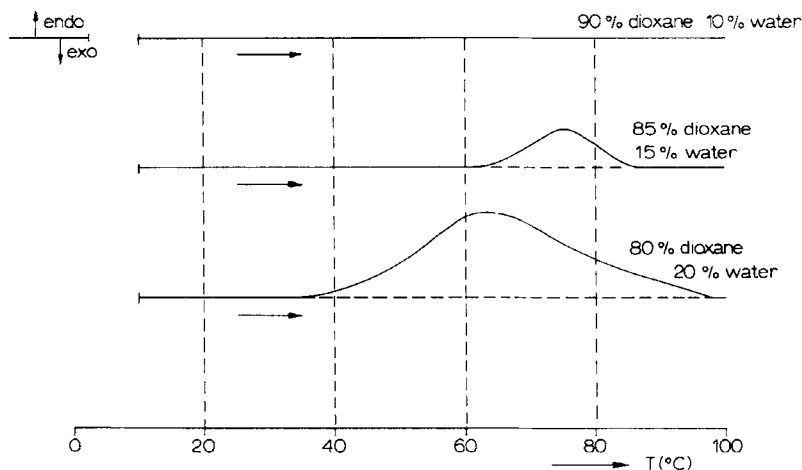


FIG. 4. DSC traces for 40% CA in mixtures of different compositions dioxane/water. Aging for 2 days at room temperature. Equal quantities in sample pans.

The effect of aging at these high polymer concentrations is demonstrated in Figure 5. The sample with a solvent mixture ratio of 80% dioxane and 20% water is cooled at a rate of  $40^{\circ}\text{C}/\text{min}$  from  $100$  to  $10^{\circ}\text{C}$ . After aging for different periods of time an endothermic effect is observed upon heating (heating rate,  $10^{\circ}\text{C}/\text{min}$ ). The appearance of this endothermic effect can be strongly influenced by the lowest cooling temperature. Cooling to  $-10^{\circ}\text{C}$  and immediately reheating gives an endothermic heat effect comparable with 1 h aging at  $+10^{\circ}\text{C}$ .

At still higher polymer concentrations (55%) endothermic effects upon heating have been found also at 10% water content. Still no exothermic effect appears upon cooling. As in the case of Figure 5 the endothermic effect moves gradually to higher temperatures as a function of the aging time. No endothermic effect is found on immediate reheating after cooling from  $100$  to  $10^{\circ}\text{C}$ . Increasing the water content in the solvent mixture to 15% gives an endothermic heat effect on immediate reheating. There is also an exothermic effect on cooling, as opposed to all the other experiments (Fig. 6). Maybe some higher melting nuclei are still present at the highest temperature,  $100^{\circ}\text{C}$ .

In general we can state that the presence of exothermic and endothermic heat effects strongly depends on the water content and the polymer concentration of the sample. Furthermore, the rate of the temperature change and the temperature to which the sample is cooled determine to a great extent the kinetics of the process under study. These kinetic effects appear in a shift in the position

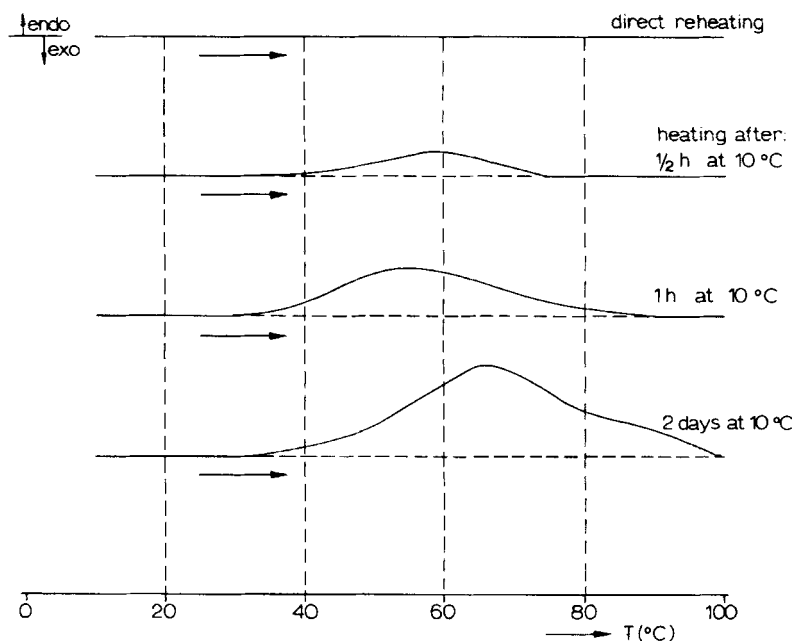


FIG. 5. Endothermic effects for 40% CA in mixture 80% dioxane/20% water after aging at  $10^{\circ}\text{C}$ , during different time periods.

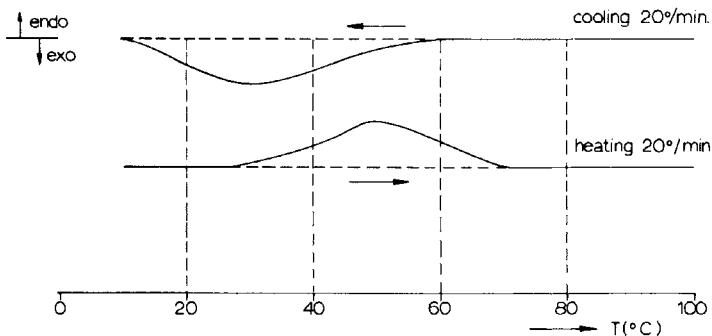


FIG. 6. Endothermic and exothermic effect for 55% CA in a mixture 85% dioxane/15% water.

of the peaks and in a change in the area under the peaks in the DSC thermograms. More experiments are necessary to reveal these kinetic aspects in full detail.

## DISCUSSION

In discussing the results reported here we must distinguish between two types of systems for which thermograms have been obtained:

(I) Polymer solutions in region I (Fig. 2) show a fast type of phase separation upon cooling, which takes place without caloric effect; after prolonged aging, however, these systems show measurable heat effects in DSC measurements upon heating.

(II) Polymer solutions in region II (Fig. 2) which do not show visible signs of phase separation upon cooling, but which show peaks in the DSC thermograms after aging.

We will discuss these systems separately.

### Polymer Solutions from Region I

For solutions of up to 20% polymer concentration and with the appropriate amount of nonsolvent in the mixture, cloud points can be measured upon cooling. Turbidity appears on cooling and disappears on heating at the same temperature. The cloud point temperatures are independent of the rate of cooling. These observations indicate a liquid-liquid type of phase separation. With DSC experiments there are no detectable heat effects during this phase separation.

Upon aging of the turbid solutions at room temperature for several hours, a clear dilute polymer phase appears on top of a cloudy, concentrated gel-like phase. This concentrated phase "melts" upon heating. In the DSC experiment this shows up as an endothermic peak. It follows from the thermograms that the melting peak falls entirely below the cloud point temperature.

From the peak area in the thermograms it can be calculated that the endothermic effect for a 10% CA solution in a dioxane (60)/water (40) mixture, after

aging for 2 days at room temperature, amounts to 9.6 J/g of solution, or 5 kJ/mol of monomer units of the polymer. This value agrees quite well with published values [15] found in gelling systems, where crystallization plays a role.

In conclusion it can be said that for solutions in region I upon cooling liquid-liquid phase separation sets in, which is a kinetically fast process. In the system under study this is followed by a slow gelation process taking place in the concentrated polymer phase. These gelled structures melt on reheating and this process can be detected by DSC experiments.

### **Polymer Solutions from Region II**

At polymer concentrations of 40–55% and fairly low nonsolvent content (10–20% of water in the solvent mixture) we do not find any visible sign of phase separation upon cooling, but again we find endothermic DSC peaks upon reheating after aging the solutions at ambient temperatures. The appearance and the area of the peaks in the thermograms can be influenced strongly by varying the polymer concentration or the nonsolvent content. Even exothermic effects may appear (Fig. 6). These effects demonstrate that gelation/crystallization occurs in these systems. For most of the solutions studied the processes leading to endothermic heat effects are rather slow, which is similar to the effects for the two-phase region I.

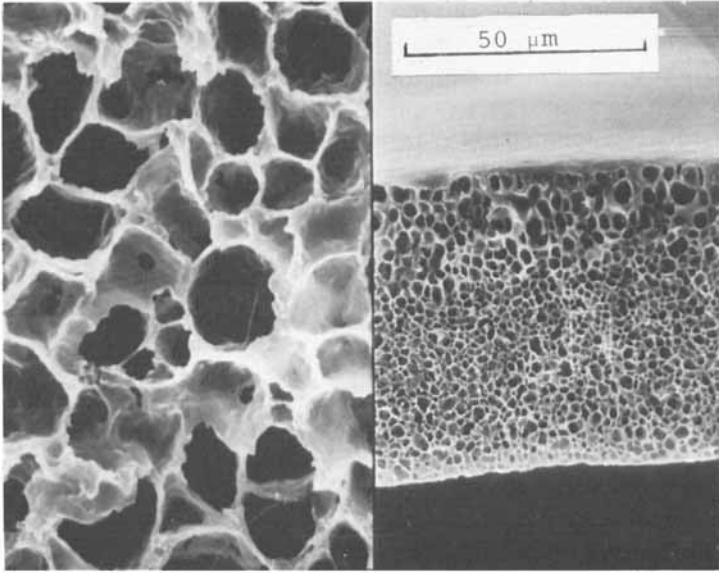
The peak areas for region II are smaller than those found in region I. The peaks found in Figure 4 correspond to values of 1.2 kJ/mol of monomer units of CA for the solution in a mixture of dioxane (80)/water (20) and only 250 J/mol of monomer units for the solution of CA in a mixture of dioxane (85)/water (15). For a CA solution in dioxane (90)/water (10) there is no endothermic peak, for the normal aging period and temperature. Probably differences in nucleation of the microcrystalline phase at different water content could explain these results, but further experimentation is necessary here.

### **Relevance to Membrane Formation**

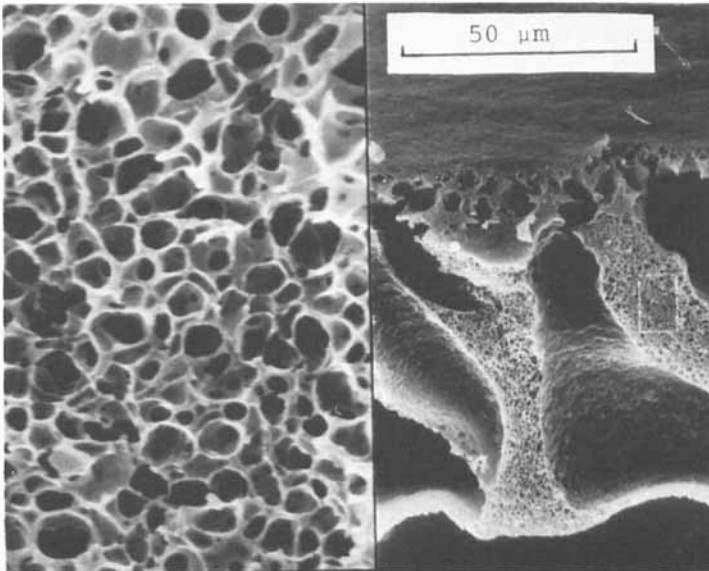
A membrane-forming system, which shows liquid-liquid phase separation for certain compositions and gelation at different, higher, polymer content, has been reported earlier by Koenhen et al. [5]. Although the polyurethane/DMF/water system, which was studied in ref. 5, is not a very practical membrane-forming system, the same two types of phase separation were found to be important for the formation of the layered structure in membranes, viz., gelation being responsible for skin formation and liquid-liquid phase separation (followed by gelation of the concentrated phase) generating the open, porous sublayer of the membrane.

Cellulose acetate is a well-known membrane material, but it appears that there are no thermodynamic or kinetic data to be found in the literature about its phase separation. The experimental results reported here show that both liquid-liquid phase separation and gelation (or crystallization) are possible for the system





(a)



(b)

FIG. 7. SEM photographs of porous substructure in membranes. The left parts give a 10X enlargement of the porous substructure. Coagulation at (a) 52°C and (b) 3°C.

CA/dioxane/water. Analogous results have been found in our laboratory for other membrane-forming systems [16].

As an illustration for the membrane structures obtainable we give two scanning electron microscope photographs of the cross section of membranes formed by casting a 10% solution of CA in dioxane as a 0.2-mm-thick film on a glass plate, and immersing the film in a nonsolvent (water) bath held at two different temperatures, 52°C [Fig. 7(a)] and 3°C [Fig. 7(b)], respectively. We note the porous structure typical for liquid-liquid phase separation, in which the pores are the regions of the dilute polymer phase, which have nucleated and grown in the second, polymer-rich phase.

### CONCLUSION

From cloud point measurements and DSC thermograms we conclude that in the system CA/dioxane/water both liquid-liquid phase separation and crystallization are possible. This is relevant to the description of the formation of the dense skin and the porous sublayer of a membrane.

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