

# Preparation of Porous PVC Membrane via a Phase Inversion Method from PVC/DMAc/Water/Additives

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**ABSTRACT:** Poly(vinyl chloride) membranes were prepared via a phase inversion method, using *N,N*-dimethylacetamide (DMAc) as solvent, polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), and sucrose as three typical additives and water as the coagulation medium. The phase diagrams of the PVC/DMAc/additives/water quaternary systems were constructed using cloud-point experimental data. With the addition of the different additives, the effect of dope solution temperature on the dope solution viscosity and the structure of membranes were inves-

tigated. It indicates that the viscosity of the PVC/DMAc dope solution with the additive increase compared with the dope solution without any additive and the addition of the additives into the dope solution alter the morphology and structure of the resultant membranes during the phase-inversion process. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 557–562, 2011

**Key words:** poly(vinyl chloride); phase diagrams; cloud point; additives; morphology structure

## INTRODUCTION

Phase inversion is a well-known process for the preparation of a wide variety asymmetric membrane,<sup>1–3</sup> which can be accomplished by nearly all kinds of techniques such as nonsolvent induced phase separation (NIPS), thermally introduced phase separation (TIPS), vapor introduced phase separation (VIPS), and evaporation introduced phase separation.<sup>4–5</sup> Poly(vinyl chloride) (PVC) is an outstanding membrane material for its stiffness, low cost, excellent physical properties as well as mechanical performance, and exceptional chemical resistance such as halogens, oxidants, inorganic acids, alkalis, and solvents. Another main advantage of PVC as a membrane material is its easy of dissolution in common organic solvents, such as *N,N* dimethylacetamide (DMAc), dimethylformamide (DMF), tetrahydrofuran (THF), and *N*-methyl-pyrrolidinone (NMP). Hence,

PVC membranes could be widely fabricated by conventional phase-inversion processes.<sup>6–7</sup>

Research and development of PVC membranes focused strongly on the fundamental membrane morphological studies via phase inversion process.<sup>8</sup> Hirose et al.<sup>9</sup> have looked into the preparation of PVC membranes and discussed the cause of phase separation process affected on the membrane structure. Bodzek and Konieczny<sup>10</sup> have investigated the morphology and separation of membranes prepared from the PVC/DMF/water system with changing the PVC molecular weight. Hiroshi et al.<sup>11</sup> have reported the fabrication of flat PVC membranes could be affected by the factors, such as casting solution compositions, polymer concentrations, solvents (DMAc, DMF, and THF), and additives (water, methanol, ethanol, and *n*-propanol). Xu et al.<sup>12</sup> have studied the morphology and performance from the PVC/DMAc/water/additives and reported that the addition of PVP or PEG could increase the membrane porosity and enhance the permeation by changing the membrane morphology. In these studies, additives PVP, PEG, and small molecular additives were introduced, aiming at improving the morphology, performance, and mechanical strength.

In this study, PEG, PVP, and small organic molecular sucrose were used as different additives in PVC/DMAc/water solution systems for the development of high performance membrane. The effect of additives on the viscosity profile and phase separation behavior of PVC/DMAc polymer solutions at different temperature was studied. The influence of

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different additives on the final PVC membrane structure was also investigated.

## EXPERIMENTAL

### Materials

PVC resins, whose average degrees of polymerization were 1000 and 1100, respectively, were obtained from Tianjin Dagu Chemical Plant (Tianjin, China). PVP ( $M_w = 40000$ ) was obtained from Boai NKY Pharmaceuticals (Tianjin, P.R. China). PEG ( $M_w = 1000$ ) and sucrose were both analytical grade. *N,N*-dimethylacetamide (DMAc, >99%) was from Institute of Membrane Science and Technique, Tianjin Polytechnic University.

### Determination of the cloud point curve

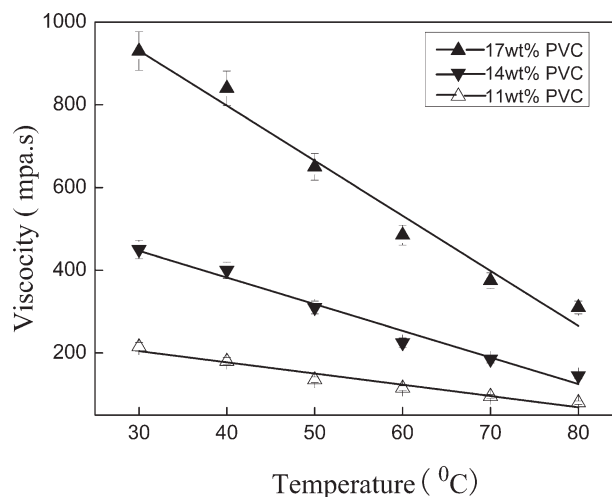
Under different temperature, water as nonsolvent was added to PVC/DMAc/additives system to investigate cloud phenomenon, which was using DMAc as solvent, PEG, PVP, and sucrose as three typical additives. Usually, cloud point data were measured by means of a titration method. The PVC/DMAc/additives solution, which is initially transparent, becomes opaque with titration of nonsolvent water. In cases where localized precipitation occurred, especially at higher polymer concentration, further addition of nonsolvent water was performed only after the solution became homogeneous phase again. This was carried out until the titration end point was reached. Based on the above titration point, the cloud point curve was constructed.

### The absolute viscosity of dope solution

The absolute viscosity of the dope solution was measured by Rotary Viscometer NDJ-7 (Tian Ping, China) at various temperatures. The dope solutions including PVC and additives (PEG, PVP, sucrose) were plenty dissolved in DMAc, and then they were poured into the proper rotor. When the temperature of the dope in the rotor was stabilized by the circulation water, the absolute viscosity data of the solution were recorded.

### Membrane preparation by the phase inversion method

Homogeneous polymer solutions of 12.5 wt % of PVC with 2.5 wt % the additives (PEG, PVP, sucrose) in DMAc were cast on glass plates with uniform thickness of 170  $\mu\text{m}$  by a glass blade. Immediately after casting, the glass plates were immersed in a coagulation bath containing distilled water at different temperature. After the formation of the flat membranes were prepared, the sample was stored



**Figure 1** The effect of temperature on the viscosity of PVC/DMAc polymer solution.

into a fresh water to remove the left solvent and then immersed into a tank containing 60% glycerol solution for at least 24 h.

### Scanning electron microscope analysis

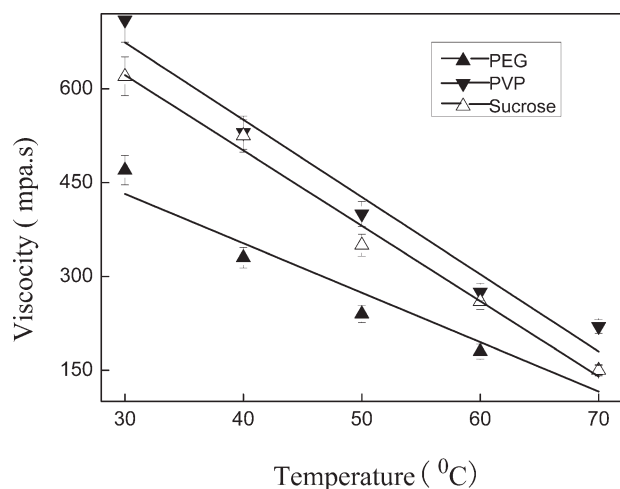
The morphology of the membranes was observed with FEI Quanta 200 (Netherlands) scanning electron microscope (SEM). The samples were broken during dipping in liquid nitrogen and sputtered with gold to keep the cross-sections structure of the samples.

## RESULTS AND DISCUSSIONS

### The effect of additives on the viscosity of the dope solution

Viscosity of the polymer dope is a key parameter to affect the kinetics of the phase inversion, which affects the structure and performance of resultant membranes. To characterize the dope with respect to the phase separation during the temperature changed, the viscosity of selected membrane-forming systems is investigated.

Figures 1 and 2 give the data of the viscosity PVC/DMAc dope solution systems with or without additives exchanged with various temperatures. Figure 1 shows the viscosities are extremely decreased in the entire range of temperature at the high concentration of 17-wt % PVC (920 mpa s) solution, whereas a smooth decrease of the viscosity with lessening content of 11-wt % PVC (220 mpa s) is observed. It is shown that the viscosity of the dope solution is strongly affected by the concentration of the polymer with the temperature changed. Figure 2 shows the diversification viscosity of the polymer dopes with different additives (PVP, PEG, and sucrose) are measured at different temperature. At



**Figure 2** The effect of temperature on the viscosity of a 11 wt % PVC solution with different additives.

30°C, the viscosities of 11 wt % PVC and 5 wt % additives (PVP and PEG) dope solutions prepared are found to follow the order of PVP > PEG, according to their molecular weights PVP ( $M_w = 40000$ ) and PEG ( $M_w = 1000$ ). The introduction of sucrose into the dope solution could also increase the viscosity of the dope, and the extent of increase is similar to the same amount of containing PVP and PEG dope solution. An increase in viscosity is seldom reported previously for PVC/DMAc/sucrose system, it may be mainly due to the formation of bridge-complexes among sucrose, polymer macromolecules, and DMAc, which deteriorate the polymer chains flexibility or cause a decrease in distributive freedom of the polymer in the dope solution.

**Effect of additives on the isothermal phase diagram**

In the phase inversion process induced by a nonsolvent, the exchange of the solvent and nonsolvent has played the important role when a homogeneous polymeric solution is initially demixed into two liquid phases.<sup>13-15</sup> The phase with the higher polymer concentration forms the solid membrane; the phase with a lower polymer concentration forms the pores of the membrane. During the process, the exchange of solvent and nonsolvent in the demixed phases continues to cause an increase of the polymer concentration in the concentrated phase surrounding the pores. The polymer molecules may rearrange their structure until the solidification (vitrification or crystallization) of the concentrated phase occurs. By controlling the initial stage of the phase inversion, the membrane morphology can be controlled.<sup>16</sup>

The phase demixing behavior during immersion precipitation can be assessed by cloud point measurements since the cloud point corresponds to the

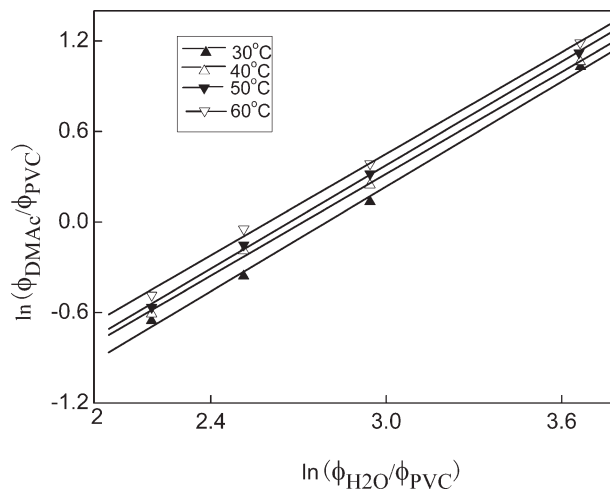
position of the binodal in a ternary phase diagram. This curve characterizes the thermodynamic properties of the membrane-forming system at the point of phase inversion and can be determined with simple turbidity measurements. To relate this data to the real membrane formation, cloud points of selected dope systems have to be determined at different polymer concentrations and temperature. Boom et al.<sup>17</sup> investigates that a linearized cloud point (LCP) correction is for composition of ternary systems consisting of one polymer, one solvent, and one nonsolvent, which correlates the concentrations in any single phase with on the range of the demixing (the cloud point).

$$\ln \frac{\phi_1}{\phi_3} = b \ln \frac{\phi_2}{\phi_3} + a \tag{1}$$

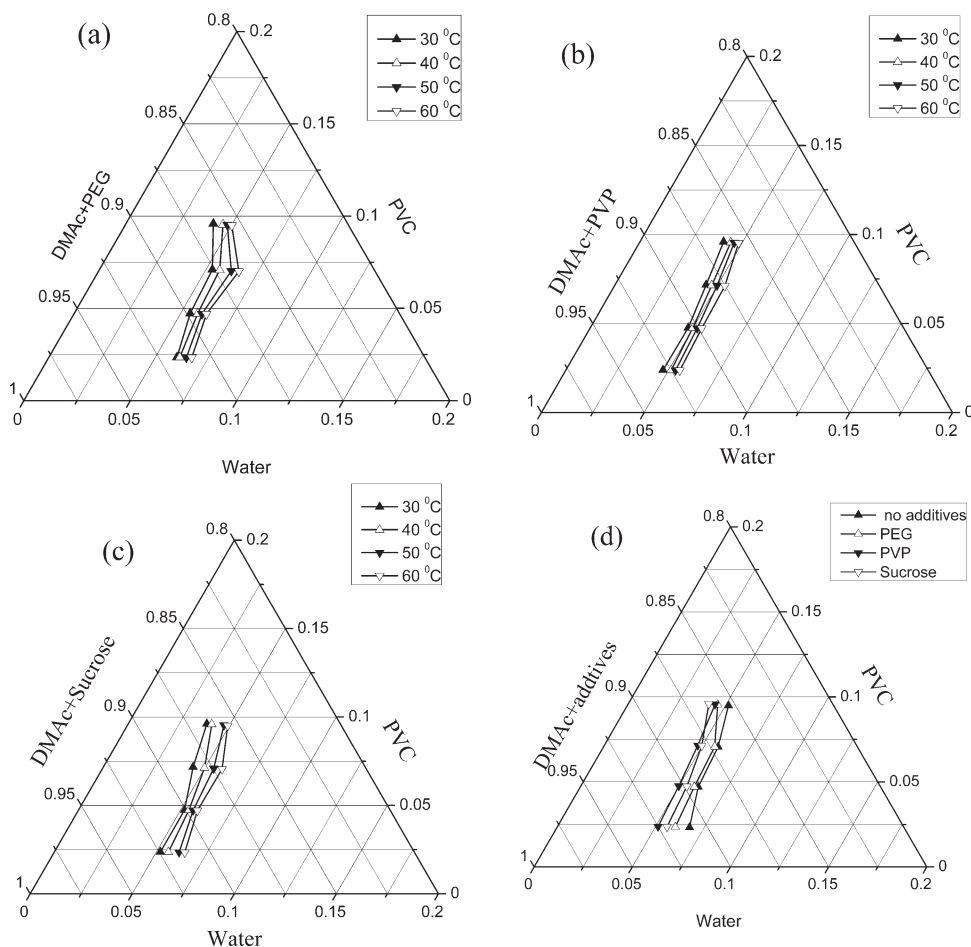
where  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  is separately indicated as the volume fraction of nonsolvent, solvent, and polymer. In this LCP relation, there are two parameters: the slope ( $b$ ) and the intercept ( $a$ ). It is reported that in  $b$  parameter the slope in the LCP is independent of the interaction parameters and only dependent on the molar volumes.

Data of the PVC/DMAc/H<sub>2</sub>O systems for different temperature are depicted in linearization as shown in Figure 3. Experimental investigations are limited to a dope solution content range from a lower concentration with 2.5 wt % PVC up to a higher content of 10 wt % PVC, since the cloud point determinations are carried out at different temperature. It is shown that the LCP cloud point with the PVC/DMAc/water system have a good linear relation at different temperature, therefore when the membrane forming system, this is a simple way to describe the liquid-liquid demixing.

From Figure 3, the slope of the PVC/DMAc/water system, which has not been effected on temperature, is just the same without the molar volumes changed.



**Figure 3** Linearized cloud point curve of the PVC/DMAc/water system at different temperature.



**Figure 4** Effects of additives on the precipitation curves of PVC/DMAC/water ternary system at different temperature [(a) PEG, (b) PVP, (c) sucrose, and (d) the cloud point data for the PVC/DMAC/water/additives at 40°C].

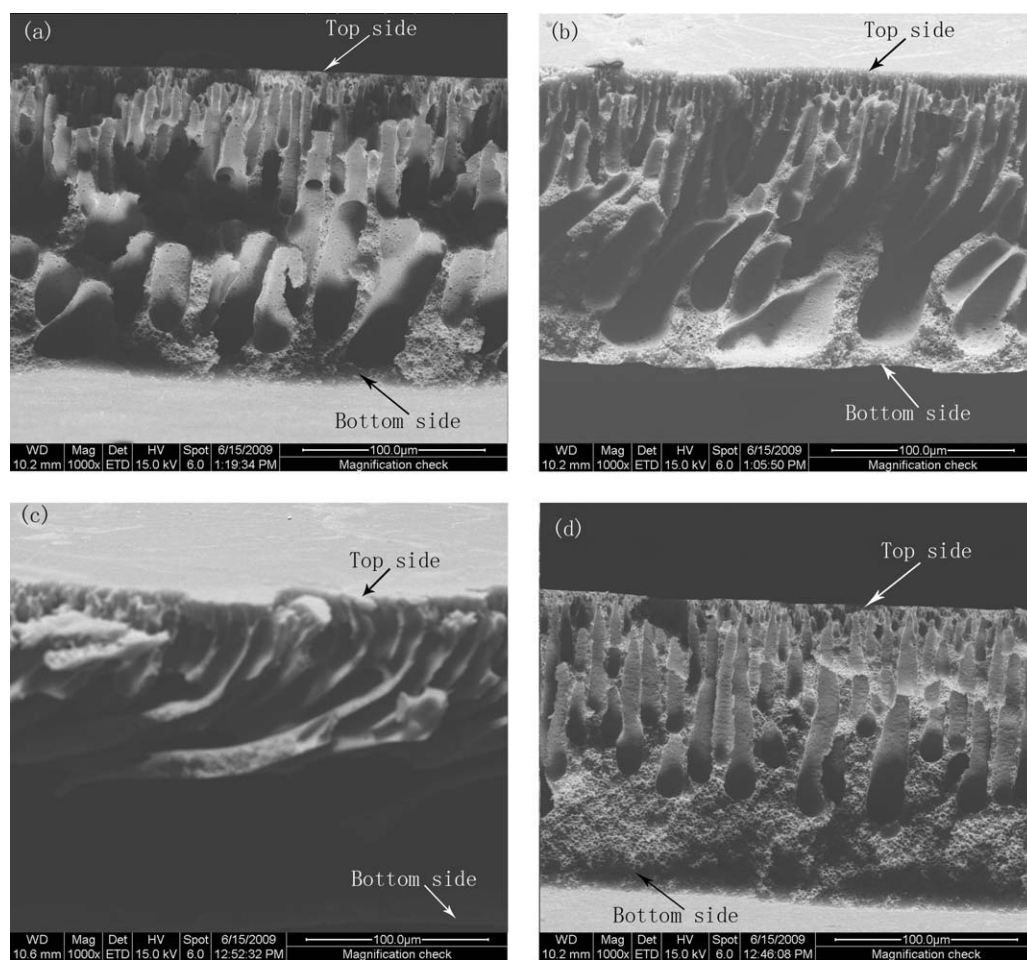
Significant differences exist in the point of interception  $a$ . The temperature of PVC/DMAC/water system increased, results in an increase of a parameter pointed out a more favorable solution state of the membrane-forming system.

Experimental data for construction of the phase diagram was obtained using a cloud-point technique, which has been described in detailed elsewhere.<sup>18</sup> In our experiment, the results demonstrated the shift of the bimodal for the PVC/DMAC/water/additives systems follow additives PEG, PVP, and sucrose, as shown in Figure 4. The effects of three additives PEG, PVP, and sucrose on the phase-inversion behavior of PVC/DMAC/water system are studied at 30, 40, 50, and 60°C. As these figures show the shift of binodal line towards the polymer-solvent axis (i.e., a reduction in the width of the one phase homogeneous region) signifies a reduced overall nonsolvent tolerance of the polymer solution system. The shift was also found that the cloud point curve of PVC/DMAC/water/additives systems was closer to the polymer-solvent axis along with the temperature decreased, and so less water was needed for the precipitation of PVC in this system

with falling of the temperature. Evidently, the effect due to the difference in the amount of polymer solution with different additives was overwhelmed by influence from the elevated solution temperature.

As the solution temperature was increased to 40°C, the binodal line was found to shift towards the right as shown in Figure 4(d), hence demonstrating a greater nonsolvent water tolerance. It was shown isothermal precipitation curves for the addition of PEG, PVP, and sucrose with different polymer concentration as well as the isothermal condition employed, based on the experiment carried out at 40°C. It was also of interest to note the overlapping of the bimodal lines for the PVC/DMAC/PEG/water system, where PVP and sucrose were used as additives. In general, the addition of additives was found to reduce the PVC/DMAC/additives systems degree of water tolerance. For the lower concentration of the PVC polymer (below 7.5 wt %) with different additives at 40°C, the impact of the 5 wt % additive used in reducing the envelope of the one-phase homogeneous region follows the trend of sucrose > PEG > PVP, as shown in Figure 4(d), which was different at the high concentration of 10 wt % PVC.





**Figure 5** The morphology of the membrane with different additives at 25°C [(a) no additives, (b) PEG, (c) PVP, and (d) sucrose].

### Effect of additives on the membrane morphology

Morphologies of the membranes prepared from water/DMAc/PVC systems with or without additives are depicted in Figure 5. It was shown that macrovoids were observed in the sublayer of all the prepared membranes. Barzin<sup>19</sup> have pointed out the presence of macrovoids proves that there is a high mutual affinity between water and DMAc solvent in these systems, this high mutual affinity between nonsolvent and solvent induces an instantaneous demixing in the aforementioned systems that leads to the formation of macrovoids in the resulting membranes structure.

The comparison was made between the morphology of membranes prepared from these systems with different additives in the dope solution at the same polymer concentration (12 wt %). SEMs of the membrane prepared from water/DMAc/PVC/additives systems cross sections were shown in Figure 5(b–d). It was indicated that the pores in the membranes prepared of solutions with different additives have nearly channel-like structures with open mac-

rovoids ends for these systems. The effect of PVP addition on the membrane morphology was shown in Figure 5(c). Compared with the morphology of the membranes prepared using PEG and sucrose dope solutions [Fig. 5(b,d)], larger finger-like pores and less sponge-like structure could be seen on the cross-section of the membranes with 5 wt % as the PVP additive. These macrovoids became more accentuated and extended over the whole cross-section when PVP was present in the casting solution [Fig. 5(c)]; on the contrary, sucrose as additive obviously reduced macrovoids formation and engenders abundance sponge-like structures extended to the bottom of the membrane [Fig. 5(d)], PEG added to the cast solution identically reduced the growth of the macrovoids [Fig. 5(b)]. These differences could be explained by the competitive thermodynamic and kinetic effect of the additives on the phase inversion process.<sup>20</sup> In the process of phase inversion, PEG, PVP, and sucrose, working as nonsolvents, have reduced the thermodynamic miscibility of the dope solution (thermodynamic effect), and induced the enhancement of liquid–liquid phase separation.

However, because the additives also could improve the solution viscosity and delay the mutual diffusion between solvent in the coagulation bath (Fig. 2) and nonsolvent in the coagulation bath; therefore, they induced a phase separation delay with different velocity (kinetic effect). Systems with PEG and PVP as the additives tended to form macrovoids with finger-like structure at a rapid phase inversion rate, whereas systems with a slow phase inversion rate result in a sponge-like structure, sucrose in the PVC polymer solution operated as an agent for suppressing macrovoid formation (kinetic effect) at a polymer concentration (12.5 wt %). The above observations were believed to be associated with the change of the thermodynamic and kinetic properties of the system before and after addition of different additives. Therefore, changing the additives in the PVC polymer systems may lead to the creation of more sponge-like structures in the prepared membranes morphology.

### CONCLUSIONS

In this work, prepared from the method of phase-inversion, the effects of three typical additives (PVP, PEG and sucrose) on the fabrication of the asymmetric PVC microporous membranes were investigated. Based on the analyses of the isothermal phase diagram for the PVC/DMAc/water system without/with an additive and the viscosity of the dope solutions, the way in which the additives affected membrane preparation was investigated in terms of membrane morphology and structure. The viscosity of the PVC/DMAc dope solution with the additive increased compared with the dope solution without any additive. It was found that the addition of PVP, PEG, and sucrose reduced the thermodynamic stability of the dope solution in reaction with water. Moreover, the gelatin velocity on thermodynamic

process of the membranes was affected by the three additives in the sequence of PVP > PEG > sucrose. Thus, the morphology and structure changes of the resultant membranes caused by the additive were believed to be associated with the change of the thermodynamic and kinetic properties of the system in the phase inversion process. A small amount of sucrose addition could change the kinetic property of the system significantly with more sponge-like structures, whereas the thermodynamic effect due to PVP may play a dominant role in determining the membrane structure with more large finger-like extended to the bottom of the membrane.

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