# Determination of Concentration Changes on Membrane Surface as Function of Time During Evaporation of Reverse-Osmosis Film Casting Solutions

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## Synopsis

Data on the activity of acetone for the binary system acetone-formamide, and a specific ternary system cellulose acetate-acetone-formamide are given for the temperature range 0 to 30°C. A method of determining concentration changes occurring on the membrane surface during the evaporation stage in the process of making cellulose acetate reverse osmosis membranes is illustrated.

## INTRODUCTION

The structure of the casting solution, solvent evaporation rate during film formation, and the film shrinkage temperature profile have emerged as important controlling parameters in the formation and development of the ultimate porous structure of the membrane surface in reverse-osmosis films.[1-4] In order to correlate membrane performance with the above parameters and establish a basis for the development of more productive reverse-osmosis membranes, it may be necessary to follow the concentration changes on the membrane surface as a function of time during evaporation (or the solvent removal stage) in the film-making process. This paper illustrates a method of determining such concentration changes with respect to membranes obtained from cellulose acetate–acetone–formamide casting solutions.[5]

The data presented here refer to membranes cast on glass plates under the following conditions: casting solution composition is the same as Batch 47-type[2] (cellulose acetate:acetone:formamide ratio is 25:45:30 wt-%); temperature of the casting solution is that of the casting atmosphere; temperature of the glass plate is the same as the laboratory temperature, namely, 24°C; the casting atmosphere is ambient air at 24°C; and the membrane area is 64.2 cm.[2]

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## EXPERIMENTAL

Three kinds of experimental data are required for the purpose. They are (1) data on the vapor pressure of acetone in acetone–formamide and in cellulose acetate–acetone–formamide solution systems, (2) data on acetone (solvent) evaporation rate under the film-casting conditions, and (3) data on the temperature on the film surface during evaporation. These data were obtained as follows, using reagent-grade acetone, practical-grade formamide (same as that used in film-casting solutions), and Eastman cellulose acetate E398-3.

### Vapor Pressure of Acetone

The vapor pressures of solutions of different compositions of the binary system acetone–formamide and of the ternary system cellulose acetate–acetone–formamide were measured at several temperatures in the range of $-25°$ to $28°C$ using an all-glass apparatus with a closed mercury manometer connected to a high-vacuum pump. Ten- to 30-g samples of the solutions were used for the measurements. To start with, the sample was frozen at liquid nitrogen temperature, held frozen for at least 1 hr, then evacuated and kept under vacuum for another hour, and finally brought back to room temperature at which it was held for at least 2 hr. This sequence of operations of freezing, evacuation, and defreezing was repeated two or three times to remove all air from the system. The vapor pressure measurements were then made under steady-state conditions using a constant-temperature bath to keep the sample at different temperatures. Since the vapor pressure of pure formamide is negligible in the temperature range studied (1 mm Hg at 70.5°C[6a]), the observed vapor pressure was considered to be derived entirely from the acetone in the solution.

### Acetone Evaporation Rate

This was obtained by determining the change in weight of the polymer film cast on a glass plate, as a function of time, following the method of Kunst and Sourirajan.[3]
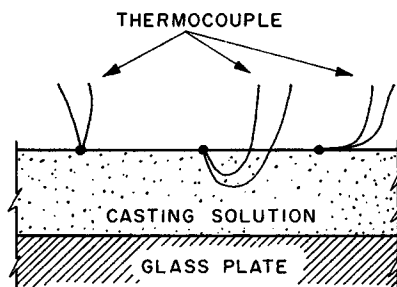


Fig. 1. Measurement of temperature on film surface.

## Temperature of Film Surface During Evaporation

A 40-gauge copper-constantan thermocouple attached to an automatic temperature recorder was used to follow the temperature changes on the film surface as a function of time immediately after casting.   The thermocouple was located on the film surface in one of three different ways shown in Figure 1, and the results obtained were essentially the same in all cases.

## RESULTS  AND  DISCUSSION

### Activity of Acetone

Figure 2 gives the experimental vapor pressure data ($p$ in mm Hg) obtained at different temperatures ($t°C$) for several compositions of acetone-
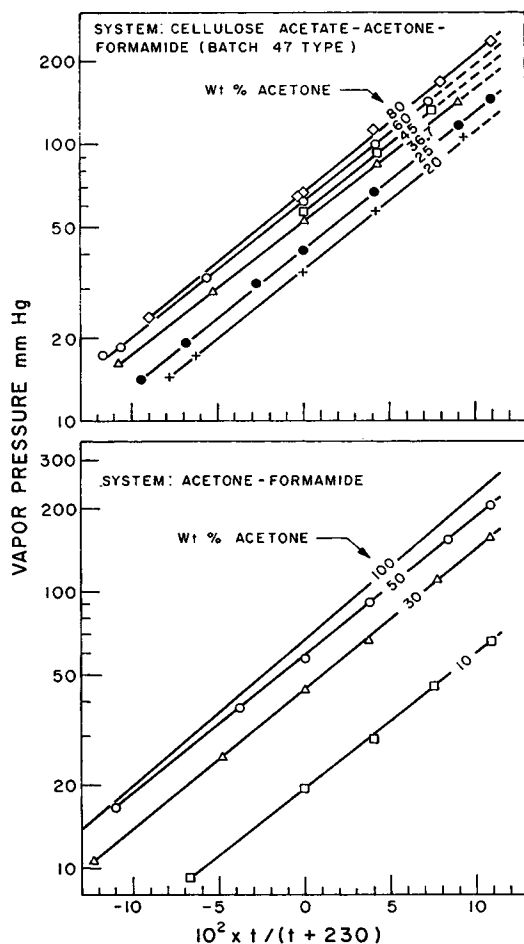


Fig. 2. Vapor pressure data for systems acetone–formamide and cellulose acetate–acetone–formamide.
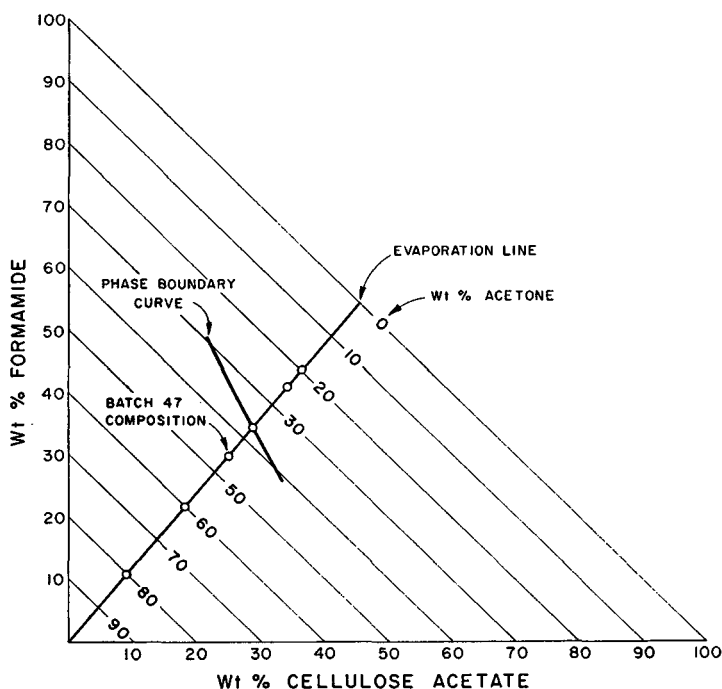
Fig. 3. Composition diagram for the system cellulose acetate-acetone-formamide.

formamide (binary) and cellulose acetate–acetone–formamide (ternary) solution systems. Following the form of Calingaert and Davis,[7] the data are plotted as log $p$ versus $t/(t + 230)$; such plots yield good straight-line correlations which permit accurate interpolation and extrapolation of experimental data in limited temperature ranges.[8] The vapor pressure data for pure acetone $(p^*)$ were taken from the literature;[6a] the data for the system cellulose acetate–acetone–formamide were obtained for five different compositions arbitrarily chosen along the evaporation line for the Batch 47-type films, as indicated in the ternary composition diagram shown in Figure 3.[9] The phase boundary curve shown in Figure 3 is that of Pilon, Kunst, and Sourirajan,[10] and it is applicable for the temperature range 0 to 30°C.

Using the vapor pressure data given in Figure 2, the activity of acetone $(p/p^*)$ can be calculated as a function of temperature and composition. Figure 4 gives a set of such activity data in the temperature range 0 to 30°C for the binary system acetone–formamide and for a specific ternary system cellulose acetate–acetone–formamide represented by the compositions lying on the evaporation line given in Figure 3, which is applicable for the Batch 47-type membranes. In calculating the mole fraction of acetone $(x)$ for the ternary system, the ratio of the weight of cellulose acetate to the molecular weight of cellulose acetate has been neglected in view of the high molecular weight of the polymer. Designating, just for identi-
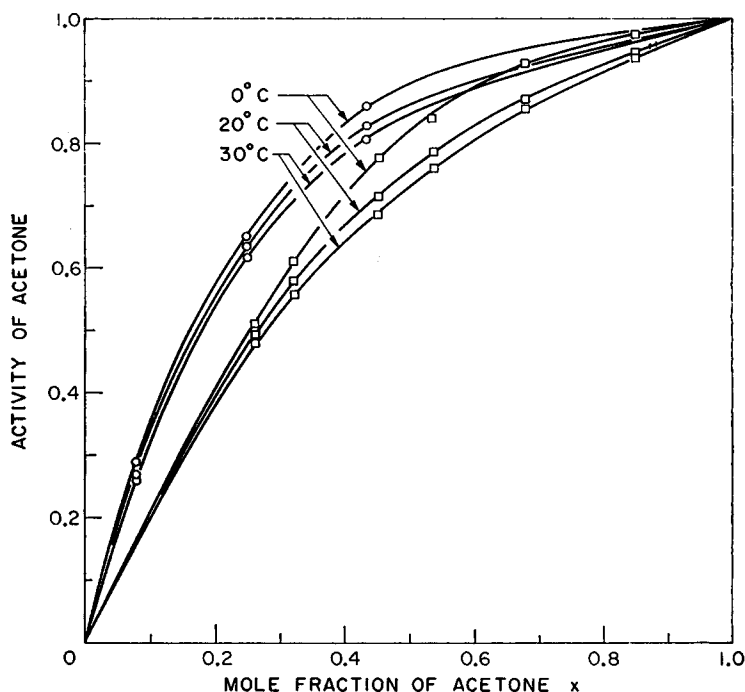
Fig. 4. Activity of acetone in the systems acetone–formamide (O) and cellulose acetate–acetone–formamide, Batch 47 type (□).

fication, cellulose acetate, acetone, and formamide as polymer, solvent, and nonsolvent, respectively, Figure 4 gives a relative measure of the interacting forces between the components of the solution systems studied, and, in particular, the data show that the solvent–nonsolvent interactions are weaker than the polymer–solvent interactions and that, in each case, such interacting forces increase with temperature.   The data given in Figure 4 can be interpolated with reasonable accuracy for practical application in reverse-osmosis membrane science.

## Evaporation of Acetone

A set of evaporation rate data was obtained by following the change in weight of 2.4 g of Batch 47-type casting solution spread on an area of 64.2 cm$^2$ on a glass plate.   From the composition of the casting solution, the weight of cellulose acetate ($w_{CA}$) on the glass plate was 0.6 g.   The weight $w$ of the polymer film left on the plate at times 15, 30, 45, 60, 75, 90, 120, 150, 180, 210, 240, 300, 360, 420, 600, 900, 1200, and 1800 sec after casting was noted.   Throughout this period, $w$ decreased, rapidly at first and slowly thereafter, owing to the evaporation of acetone into the atmosphere.   After 1800 sec, however, $w$ increased slowly and slightly, probably because of the absorption of moisture from the atmosphere on the film surface.   The
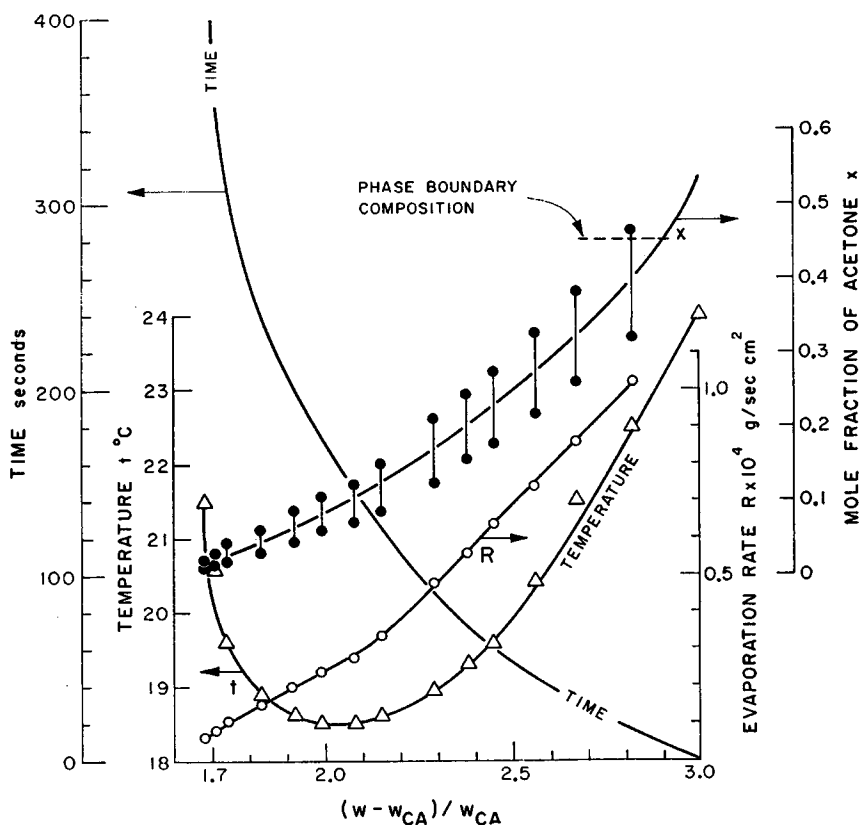
Fig. 5. Illustration of surface concentration profile during evaporation stage in reverse-osmosis film making process.

calculations illustrated below extend to the first 420 sec during which period the probable absorption of moisture, if any, was considered negligible.

From the time-versus-$w$ data, the acetone evaporation rate $R$, in g/sec-cm$^2$, and the corresponding quantity $(w - w_{CA})/w_{CA}$ were calculated as a function of time. These data are given in Figure 5, which shows that the plot of $(w - w_{CA})/w_{CA}$ versus $R$ is the familiar drying rate curve corresponding to the falling rate period, consisting of a zone of unsaturated surface drying and a zone where the internal liquid diffusion controls.[6c] Even though the data given are entirely in the falling rate period, they probably include an initial constant rate period also. A constant rate period has been observed in several other sets of data not reported here.

## Temperature on Film Surface

This depends on the details of the conditions of film casting and solvent evaporation such as thermal conductivity of the casting surface and stillness of the air in the casting atmosphere. Consequently, the temperature of the film surface is best determined experimentally. In particular, the

generalized correlation available for heat and mass transfer by forced convection[6b] does not seem applicable for calculating the temperature of the film surface from evaporation rate measurements.

Figure 5 gives the experimental data on the temperature of the film surface as a function of time under film-casting conditions same as those used for evaporation rate measurements. Ideally, both evaporation rates and surface temperatures should be determined simultaneously. Even though this could not be done because of experimental difficulties, the data presented here are considered sufficiently valid for practical purposes. The initial temperature of the film surface was assumed to be that of the casting solution (24°C), and the temperature was found to drop to 18.5°C before it rose again.

## Acetone Concentration on Membrane Surface

The rate of acetone evaporation, $R$, from the membrane surface may be expressed by the relation

$$R = k_G(p - p_{eq}) \qquad (1)$$

where $p$ and $p_{eq}$ represent, respectively, the vapor pressure of acetone for the solution system at the temperature of the membrane surface and the equilibrium vapor pressure of acetone in the casting atmosphere, and $k_G$ is the proportionality constant. For the illustrative data under consideration, $p_{eq}$ may be assumed equal to zero, so that eq. (1) becomes

$$R = k_G p. \qquad (2)$$

Assuming $k_G$ remains constant throughout the heat transfer-mass transfer process taking place on the membrane surface, the surface concentration of acetone as a function of time can be calculated as follows, using eq. (2) and the data given in Figures 2 and 4:

Calculate $k_G$ from initial values of $R$ and $p$. For the data under discussion, these values are, respectively, $1.15 \times 10^{-4}$ g/sec-cm$^2$ (estimated) and 163 mm Hg for Batch 47 composition assuming a surface temperature of 24°C. Consequently, $k_G = 7.055 \times 10^{-7}$ g/(sec cm$^2$ mm Hg).

At any given time, from the experimental values of $R$ and the surface temperature, calculate the activity of acetone on the membrane surface. For example, at 45 sec after casting, $R = 0.743 \times 10^{-4}$ and $p = 0.743 \times 10^{-4}/7.055 \times 10^{-7} = 105.3$ mm Hg. At 20.4°C (surface temperature), $p^* = 182$ mm Hg (from Fig. 2). Hence, the activity of acetone on the membrane surface is $105.3/182 = 0.579$.

Using Figure 4, determine the mole fraction of acetone ($x$) on the membrane surface corresponding to the activity of acetone calculated above. There is some question as to whether the solution on the membrane surface should be treated as a binary system (acetone–formamide) or a ternary system (cellulose acetate–acetone–formamide). For the example given

above, the values of $x$ are 0.215 and 0.325 for the binary and ternary systems, respectively.

The surface concentrations of acetone ($x$) as a function of time are also plotted in Figure 5. The lower and upper values correspond to the activity data for the binary and the ternary systems, respectively. Until the phase separation (polymer precipitation) starts, the solution on the membrane surface should be treated as a ternary system. Figure 3 shows that at the point of intersection of the phase boundary curve and the evaporation line, the concentrations of acetone and formamide are, respectively, 36.7 and 34.5 wt-%, corresponding to $x = 0.452$. Figure 5 shows that this value of $x$ occurs 19 sec after casting, based on the activity data for the ternary system. Therefore, one may conclude that phase separation on the membrane surface occurred 19 sec or less after casting for the particular case illustrated in Figure 5. For a closer estimate, one needs more data during the first 15 sec after casting. Thus, the procedure outlined above allows one to follow the concentration changes occurring on the membrane surface during the evaporation stage of the film-casting process and to estimate the time at which polymer phase separation begins.

The results given in Figure 5 correspond to the casting conditions commonly used in making the particular type of reverse-osmosis membranes discussed. Extensive data on the performance of such membranes are already available in the literature.[11] Table I gives a set of data obtained with the above membranes. Similar performance data are needed corresponding to different film-casting conditions (involving different evaporation rates and surface temperatures during film formation) in order to develop

TABLE I
Data on Membrane Performance[a]

| NaCl concentration in feed, wt-% | Operating pressure, psig | Solute separation, % | Membrane flux, gal/(day ft²) |
|---|---|---|---|
| 0.35 | 250 | 80 | 14.0 |
| | | 90 | 11.2 |
| | | 95 | 10.1 |
| 0.50 | 600 | 80 | 49.7 |
| | | 90 | 36.5 |
| | | 95 | 30.3 |
| 2.84 | 1500 | 80 | 68.4 |
| | | 90 | 52.8 |
| | | 95 | 45.1 |

[a] Film casting details: casting solution composition, cellulose acetate (E-398-3), 25 wt-%, acetone, 45 wt-%, formamide, 30 wt-%; temperature of casting solution, 24°C; temperature of casting atmosphere, 24°C; casting atmosphere, ambient air; solvent evaporation period, 30 sec; gelation medium, ice-cold water; nominal film thickness, 0.005 in. Reverse-osmosis experiments were carried out with aqueous NaCl feed solutions under conditions corresponding to a mass transfer coefficient on the high pressure side of the membrane equal to $45 \times 10^{-4}$ cm/sec.

useful correlations to serve as a basis for reverse-osmosis membrane development.

## CONCLUSIONS

The foregoing discussion illustrates the need for and the utility of experimental data on solvent activity, evaporation rate, and surface temperature relating to the film-casting process. Correlations of such data with other parameters controlling membrane performance should be undertaken for all casting solutions of practical interest. For the particular case illustrated, if, instead of a glass plate, a metal plate is used for film casting, the temperature drop would be a little less and the evaporation rate would be a little more. The net effect of these changes may or may not have a significant effect on the concentration profile on the membrane surface during evaporation and on the subsequent performance of the membrane in reverse osmosis. Such and related aspects of reverse-osmosis membrane science need detailed investigations.

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