

# Thermodynamic and Mechanistic Characterization of Water Sorption in Homogeneous and Asymmetric Cellulose Acetate Membranes

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## Synopsis

The water sorption isotherms for homogeneous and asymmetric cellulose acetate membranes have been measured at different temperatures. Subtle differences between the water sorption isotherms for asymmetric and homogeneous membranes have been interpreted by suggesting that capillary condensation contributes significantly to sorption in asymmetric membranes at high activities and also to an intriguing excess sorption observed in homogeneous membranes at intermediate activities. This model has been supported by the experimentally determined values of the enthalpy and entropy changes associated with sorption.

## INTRODUCTION

During the late fifties, Reid and Breton<sup>1</sup> observed that homogeneous cellulose acetate (CA) membranes were approximately one hundred times more permeable to water than to salts. Parallel to these investigations with homogeneous CA membranes, Loeb and Sourirajan<sup>2</sup> developed modified or so called "asymmetric" CA membranes possessing the same high salt rejection as the homogeneous membranes but a much higher permeability to water.

The extremely high permeability of asymmetric membranes generated a great deal of interest in the detailed characterization of their structure. Under the electron microscope, the asymmetric membranes appeared to consist of a fine-pored matrix with a very thin, dense layer of CA on the air-dried surface.<sup>3,4</sup> This extremely thin, dense layer was estimated to be about 0.05–0.3  $\mu\text{m}$ , whereas the overall membrane thickness is, typically, in the 100- $\mu\text{m}$  range. The porous substructure was estimated to have pore diameters mainly in the order of 0.1  $\mu\text{m}$ . Electron-microscopic studies did not suggest the presence of pores in either the homogeneous membranes nor in the dense layer of asymmetric membranes.

In addition to membrane characterization, the distribution of water within the membranes has been of interest since the transport of water and hydrated salt across the membrane in dialysis and hyperfiltration (reverse osmosis) is clearly related to the detailed state of aggregation of the transported species.

Lonsdale et al.<sup>5</sup> measured the water sorption, in asymmetric and homogeneous membranes, as a function of relative humidity. They observed no significant differences between the water sorption isotherms in homogeneous

and asymmetric CA membranes at low relative humidities, but more water was dissolved in the asymmetric CA membranes, under corresponding conditions, at relative humidities above 60%. The authors concluded that this "excess" water is due to capillary condensation within pores of the supporting substructure. Assuming that the homogeneous membranes are completely nonporous and, moreover, assuming cylindrical pores in the sublayer of the asymmetric membranes, they estimated that the distribution of pore radii within the porous substructure of the asymmetric membranes was bounded by 0.01  $\mu\text{m}$  and 0.5  $\mu\text{m}$ .

Williams et al.<sup>6</sup> compared the gravimetrically determined values of the water solubility in several polymers with the calculated ratio of the permeability divided by the independently determined diffusion coefficients. The experimental findings were interpreted in terms of the Zimm-Lundberg model<sup>7,8</sup> describing the clustering of water molecules in polymers. For the system water/cellulose acetate, they found limited, albeit measureable, clustering. Orofino et al.<sup>9</sup> extended this analysis by demonstrating the interrelationship between the Zimm-Lundberg description of the chemical potential and the Flory-Huggins<sup>10</sup> description of the chemical potential for species dissolved in polymer matrices. Other investigators<sup>11,12</sup> have calculated values of useful thermodynamic functions. For example, the partial molar enthalpy change for sorption  $\Delta\bar{H}$ , the partial molar entropy change for sorption  $\Delta\bar{S}$ , and the partial molar Gibbs free energy change for sorption  $\Delta\bar{G}$  have been determined from the sorption isotherms and the temperature dependence of the sorption isotherms for several water-polymer systems. Only limited thermodynamic data of this type are available, however, for the asymmetric CA membranes used in hyperfiltration.

Although Lonsdale et al.<sup>5</sup> have determined sorption isotherms which provide additional support for the "thin skin-porous support" characterization of an asymmetric cellulose acetate hyperfiltration membrane, no systematic study of the temperature dependence of the water sorption isotherms in CA have been reported. Stannett, Hopfenberg, et al. have, however, studied the temperature dependence of sorption equilibria in novel modifications of cellulose<sup>13</sup> and have also obtained equilibrium water sorption data in cellulose acetate<sup>14-16</sup> which are consistent with the values reported by Lonsdale et al.

It is the purpose of this paper, therefore, to provide additional support for these early models by characterizing the temperature dependence of the water sorption equilibria in homogeneous and asymmetric CA membranes. These data are interpreted in the context of previously suggested analytical and conceptual models and the well established thermodynamics of capillary phenomena.

Clearly, the choice of model used to describe the concentration dependence of a chemical potential is rather arbitrary and should be guided by ancillary characterizations and ultimate application of the analysis. In this regard, the Flory-Huggins description, the Zimm-Lundberg description, an activity coefficient, or a BET model may be preferred for interpreting specific equilibrium sorption data. Superimposed upon these analyses is the possibility of multiphase phenomena involving, typically, capillary condensation. The various models have been considered in the interpretation of the sorption data reported here.

## EXPERIMENTAL

The homogeneous CA membranes used were cast from acetone or chloroform solutions of 39.1% acetyl content CA (Cellit K 700 of Bayer Company, Leverkusen, Germany). The weight ratio of Cellit:solvent in the casting solution was 1:9. The resulting dry membrane thickness was about 30  $\mu\text{m}$ . The asymmetric membranes were cast from a ternary solution of Cellit K 700 in a mixture of acetone and formamide. The casting solution had the following composition: Cellit:formamide:acetone = 22.5:35:42.5 wt-%. The overall thickness of the asymmetric membranes was about 100  $\mu\text{m}$ . The membranes were not annealed, however, they were soaked for one week in a water bath at room temperature. Sorption isotherms were subsequently obtained by desorbing to a predetermined humidity. This technique was adopted to eliminate the possibility of "history effects" which would be incurred by prior desiccation of the sensitive membrane structures. The membranes were, therefore, subsequently contacted with water vapor at the various humidities of interest in an air-conditioning system maintaining humidity and temperature constant within  $\pm 0.8\%$  and  $\pm 0.2^\circ\text{C}$ , respectively. Samples, 200 mg each, were placed in a nonsorbing container of a thermogravimetric balance (manufactured by Linseis Company, Selb/Oberbayern, Germany). The sample weight was thereby recorded at room temperature as a function of time to monitor, initially, the water loss of the membrane sample by evaporation after the sample had been taken out of the air-conditioning system. A constant water loss by evaporation was observed during a period of about 10 min. Depending upon the water content of the sample, the water loss by evaporation varied between 0 and 1.5 mg/min. Thus, the true water content of the sample could be determined by extrapolating the linear water content-time relationship to zero time, which corresponds to the moment of removing the membrane sample from the air-conditioning system.

After having recorded the water content as a function of time at room temperature, the balance system was heated to  $115^\circ\text{C}$  in order to desiccate the membrane sample. After a drying time of about 6 hr, the recorded sample weight essentially achieved desorption equilibrium. The difference in weight between the wet and dry membrane sample permits ready calculation of the water sorbed by the membrane. The experimental findings represent mean values obtained by averaging over at least three independent determinations of desorption equilibrium. The accuracy of the experimental results are within  $\pm 5\%$  of the equilibrium value at a regain of 1 mg absorbed water per 100 mg of membrane sample, and the accuracy improves to  $\pm 1\%$  at regains beyond 3.5 mg absorbed water per 100 mg of membrane sample. Membranes from different batches absorbed equal amounts of water, indicating that the casting procedure is reproducible within the error of measurement.

The membrane samples used to obtain the regain at complete saturation were conditioned in a water bath at the corresponding temperature ( $35.2^\circ\text{C}$ ,  $40.0^\circ\text{C}$ , and  $45.1^\circ\text{C}$ ) for one week. The water adhering to the membrane surface was blotted off,<sup>17</sup> and the wet weight of the corresponding samples was measured with an analytical balance (Sartorius, accurate to  $\pm 0.1$  mg, manufactured by Sartorius Company, Göttingen, Germany). Samples as large as 1 g were used in order to minimize the normalized weighing error. The re-

ported sample weights at saturation are an average of ten single weight determinations, yielding a mean error of  $\pm 1\%$  of the equilibrium value. Thereafter, the membrane samples were dried over  $P_2O_5$  at  $115^\circ C$  for about 200 hr and the "dry weight" was determined. The experimental results, obtained for the regain at saturation, are in very good agreement with results of other investigators.<sup>5,18</sup>

## RESULTS AND DISCUSSION

No measurable differences were observed between the water sorption isotherms of homogeneous membranes cast from chloroform or acetone solutions. Therefore, only the experimental findings for homogeneous membranes cast from chloroform solutions are reported and used.

As can be seen from Figures 1 and 2, there is decidedly more water sorbed by an asymmetric membrane than by a homogeneous one at higher water activities. Since capillary structures have been suggested by electron microscopy for the asymmetric membranes,<sup>3,19,20</sup> one might reasonably assume that this "excess" water in the asymmetric membrane is confined to well-defined capillaries. The water sorption isotherm for the asymmetric membrane is nearly identical to the isotherm characterizing equilibrium sorption in the

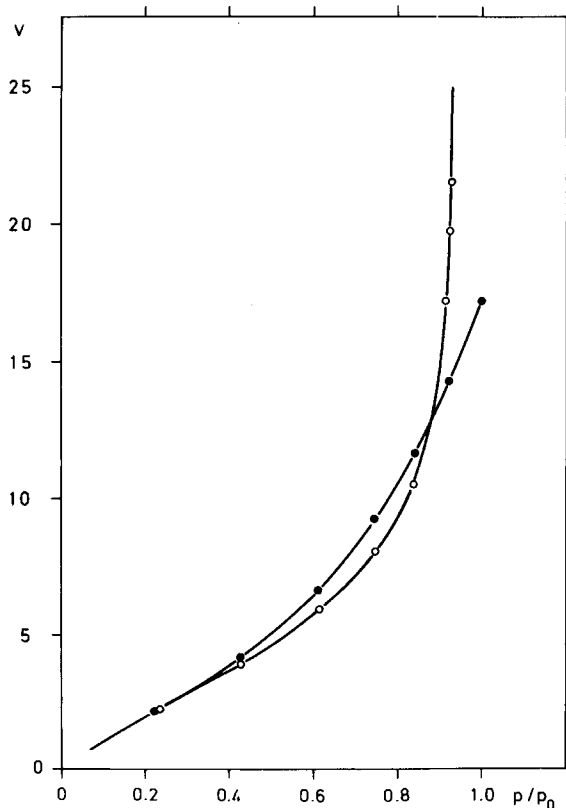


Fig. 1. Desorption isotherms of a homogeneous (●) and an unannealed asymmetric (○) cellulose acetate membrane at  $35.1^\circ C$ . Regain  $v$  in mg sorbed water per 100 mg dry membrane.

homogeneous membrane at very low relative humidities, however, "excess" water is dissolved in the homogeneous membrane at intermediate humidities.

This intriguing observation might be considered to be a consequence of condensation at intermediate humidities in the homogeneous membranes in capillaries bounded by quite specifically defined pore radii. Although one might reasonably expect some significant asymmetric distribution of pores in a "homogeneous" membrane (e.g., smaller pores in the air-dried surface), these equilibrium experiments will not discern between symmetric and asymmetric structures. Assuming cylindrical pores, the specific pore size corresponding to the relative humidity values in question is given by eq. (1):

$$RT \ln (p/p_0) = -(2\nu\sigma/r) \cos \theta \quad (1)$$

where  $R$  = absolute gas constant (erg/mole-degree),  $T$  = absolute temperature ( $^{\circ}\text{K}$ ),  $\nu$  = partial molar volume of water in the pores ( $\text{cm}^3/\text{mole}$ ),  $\sigma$  = surface tension between water and air ( $\text{erg}/\text{cm}^2$ ),  $\theta$  = contact angle between capillary wall, liquid, and vapor phase,  $r$  = pore radius (cm), and  $p/p_0$  = activity of water at temperature  $T$ .

The pore size distribution may, therefore, be calculated by combining the results of eq. (1) with the geometric constraints and the measured excess water sorbed at the respective humidity. With  $\nu = 18 \text{ cm}^3/\text{mole}$  and  $\cos \theta = 1$

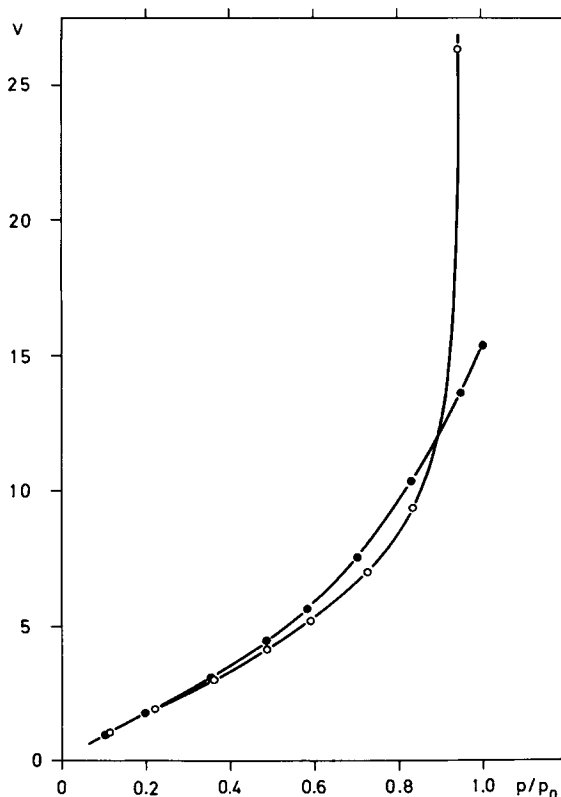


Fig. 2. Desorption isotherms of a homogeneous (●) and an unannealed asymmetric (○) cellulose acetate membrane at  $45.1^{\circ}\text{C}$ . Regain  $v$  in mg sorbed water per 100 mg dry membrane.

( $\theta = 0^\circ$ ) one, therefore, obtains  $V_r$ , the excess water corresponding to the capillary radius which would satisfy eq. (1) at the various humidities as a function of the corresponding pore radius.

These results are presented graphically in Figure 3. These calculations suggest that the so-called "homogeneous" CA membranes may, in fact, contain capillary pores which contribute significantly to the observed sorption. For relative humidities corresponding to pore radii up to  $0.004 \mu\text{m}$ , the homogeneous membrane sorbs more water than the asymmetric one. Assuming a strict capillary condensation model, these data would suggest that the homogeneous membrane may possess pores up to  $0.004 \mu\text{m}$  radius, whereas the asymmetric membrane may possess pores mainly within the range of  $0.01\text{--}0.3 \mu\text{m}$  radius. One might also conclude, therefore, that pores with diameters of the same order of magnitude may also exist in the dense skin of asymmetric membranes. Since the dense layer is extremely thin compared with the overall membrane thickness, the water confined to pores in the skin would be virtually immeasurable. These same pores, however, may contribute significantly to the transport behavior of hyperfiltration membranes.

These experiments do not, however, distinguish between pores which are present in the dense skin from those pores which are present in the largely porous sublayer. One would suspect, however, that the larger pores are essentially confined to the supporting sublayer in asymmetric membranes. These results are in general agreement with the results of electron microscopy and the values that Lonsdale et al.<sup>5</sup> calculated from their water sorption data at high humidities. Lonsdale et al. have not, however, observed the excess water sorption at intermediate activities which is observed here. These subtle differences from Lonsdale's results may, in fact, be a consequence of varia-

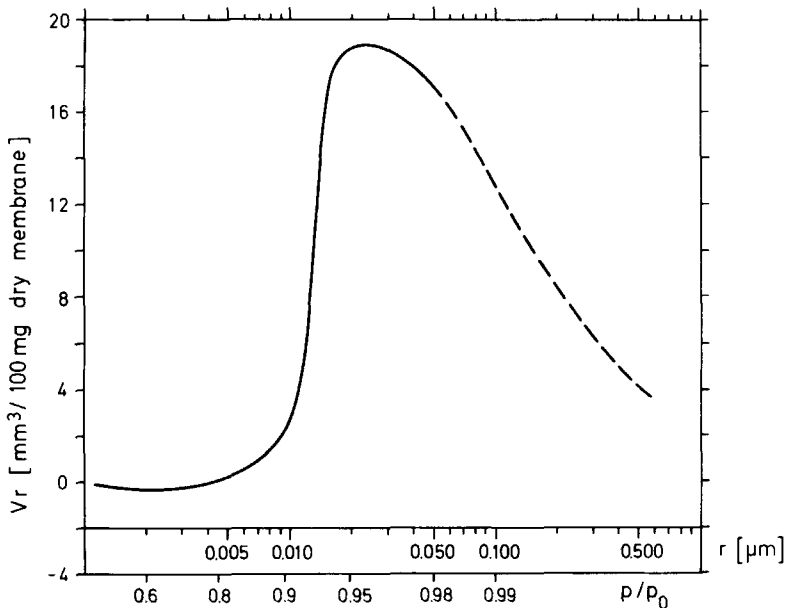


Fig. 3. Excess water sorbed at relative vapor pressures by an unannealed asymmetric membrane as a function of activity  $p/p_0$ . Corresponding calculated pore radius  $r$  is given as a second abscissa. Negative  $V_r$  corresponds to excess water in the homogeneous membrane.

tions in casting procedures and/or differences between molecular weight, degree of acetylation, and distribution of these structural parameters which may exist between the CA materials used in the respective studies.

Using the water sorption measurements over the range of temperatures from 35° to 45.1°C, and assuming ideal gas behavior for the vapor phase, the thermodynamic functions relating to sorption can be calculated by the following equations:

$$\Delta\bar{G} = RT \cdot \ln(p/p_0) \quad (2)$$

$$\Delta\bar{H} = R \cdot d\{\ln(p/p_0)\}/d(1/T) \quad (3)$$

$$\Delta\bar{S} = (\Delta\bar{H} - \Delta\bar{G})/T. \quad (4)$$

These thermodynamic functions describe the change in the respective partial molar quantity for dissolved water when 1 gram-mole liquid water is equilibrated with a very large mass of CA at a vapor pressure  $p$  and a temperature  $T$ . Condensed water at its saturation pressure  $p_0$  and at a temperature  $T$  are selected as the reference state. The enthalpy of sorption  $\Delta\bar{H}$  is calculated from the slope of the sorption isosters ( $\ln(p/p_0)$ -versus- $1/T$  plot). This plot was approximately linear (see Fig. 4) in agreement with similar experimental results of Jeffries and Wiegerink.<sup>11,12</sup> The calculated values of the thermodynamic functions are graphically shown in Figure 5. These overall values of the thermodynamic functions of water sorption might be considered as linear combinations of the partial molar quantities describing dissolution and capillary condensation, respectively. For  $\Delta\bar{G}$ , for instance, the following linear combination holds:

$$\Delta\bar{G} = x_d \cdot \Delta\bar{G}_d + x_c \cdot \Delta\bar{G}_c \quad (5)$$

where  $x_d$  = mole fraction of dissolved water,  $x_c$  = mole fraction of water

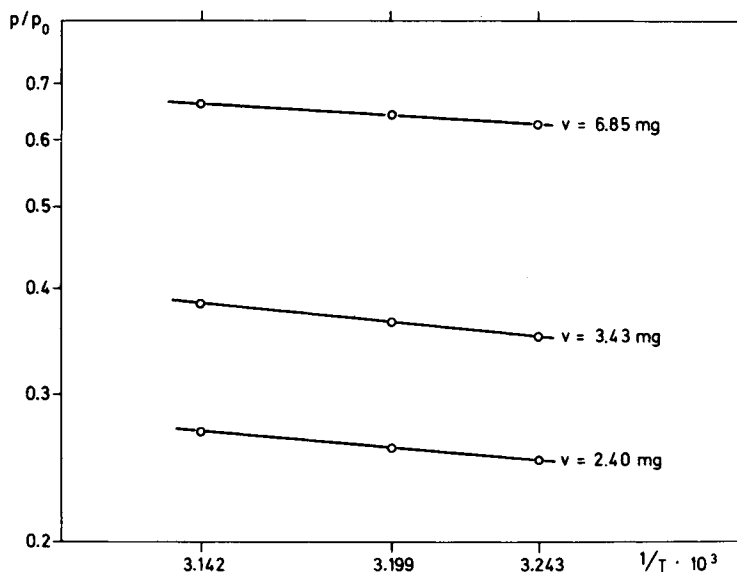


Fig. 4. Desorption isosters at several regains  $v$ .

sorbed by capillary condensation,  $\Delta\bar{G}_d$  = partial molar Gibbs free energy of dissolution, and  $\Delta\bar{G}_c$  = molar Gibbs free energy of capillary condensation.

The contribution of capillary condensation to the enthalpy and free-energy changes associated with sorption only becomes significant, however, at extremely small pore radii since the values of these thermodynamic functions are inversely related to pore radii through eqs. (1), (2), and (3). At high relative humidities (large equivalent pore radii), the contribution of capillary condensation to the numerical values of these functions (as defined) approaches zero. At extremely low water activities, however, the fraction of water taken up by capillary condensation is very small compared to the dissolved water and can, therefore, be neglected to a first approximation.

Thus, in these limiting cases, the calculated values of the thermodynamic functions are described entirely by dissolution. Since only pores of  $r < 0.01 \mu\text{m}$  are presumed to exist in the homogeneous membrane, no significant capillary condensation would occur at high water activities ( $p/p_0 > 0.9$ ). Increasing regain at higher activities is due entirely to molecular dissolution in the homogeneous membrane. The calculated enthalpy of sorption for the homogeneous membrane is approximately  $\Delta\bar{H} = -950 \text{ cal/mole}$  in this activity range, suggesting strong water-CA interactions associated with molecular dissolution.

The calculated values of the thermodynamic functions,  $\Delta\bar{G}$ ,  $\Delta\bar{H}$ , and  $\Delta\bar{S}$ , presented in Figure 5 are quite consistent with the overall interpretation of the subtle, albeit significant, differences between the various sorption isotherms. Specifically, the more exothermic absorption, apparent in the homogeneous membranes in the higher humidity range where molecular solution predominates, is consistent with the suspected strong penetrant-polymer interactions between water and CA. Moreover, the discernible decrease in the entropy of sorption for the homogeneous membrane, at intermediate activities, is consistent with the increased order imposed by capillary imbibition in this region.

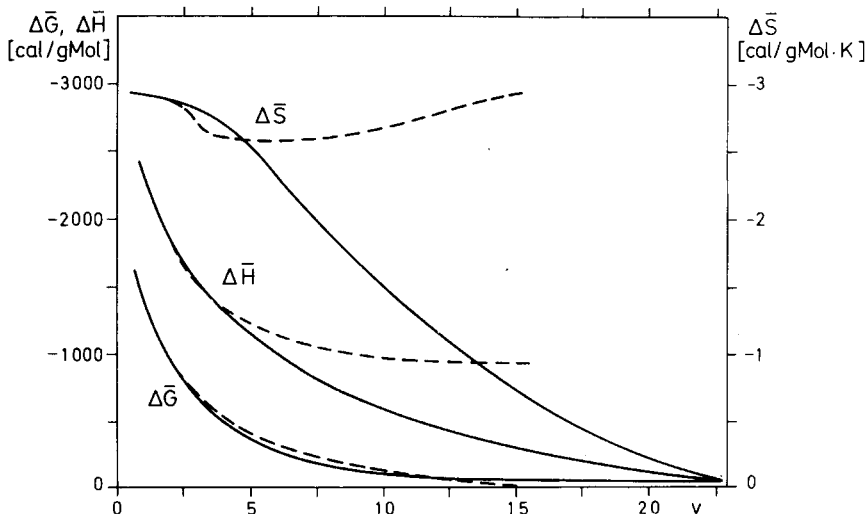


Fig. 5. Thermodynamic functions to water sorption of a homogeneous (---) and an unannealed asymmetric (—) cellulose acetate membrane as a function of regain  $v$ .



In summary, the notion of capillary condensation of water vapor, at high activities in asymmetric membranes, has been extended to explain the intriguing results presented here relating to excess water sorption in homogeneous membranes at intermediate activities. Whereas asymmetric membranes are presumably characterized by large pores, the distribution of pore sizes which would account for these surprising results in homogeneous membranes are of a much smaller characteristic size. These results, in a rather provocative way, suggest that subtle variations in structure of homogeneous CA membranes may, in fact, be present and will, in turn, affect hyperfiltration performance.

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