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A NEUTRON SPECTROSCOPIC STUDY OF THE
DIFFUSIVE KINETICS AND INTERACTIONS OF
WATER IN DENSE LAYER DESALINATION
MEMBRANES

G. J. Safford, et al

Union Carbide Corporation

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United States Department of the Interior



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To complement the neutron scattering results, differential scanning calorimetric measurements were made to determine the transitions characteristic of the "dense layer" materials. The relationship between these transitions and the membrane morphology as well as variations that result from different casting techniques and heat treatment are discussed.

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OF THE DIFFUSIVE KINETICS AND
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LAYER DESALINATION MEMBRANES

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

TABLE OF CONTENTS

	Page
ABSTRACT	1-a - 1-c
I. INTRODUCTION	2
II. EXPERIMENTAL	4
1) Instrumental	4
2) Development of Experimental Techniques and Sample Preparation	5
3) Analysis of Data	7
III. RESULTS AND DISCUSSION	8
1) Review of Background Information	8
A. The Diffusion Process for Water in Membranes	8
B. Effects of Temperature	14
C. Variations in Molecular Weight	15
2) Neutron Spectra of Water in "Dense Layer" Membrane	15
3) Effects of Temperature on the Bonding of H ₂ O Mole- cules in "Dense Layer" Materials	20
4) The Dependences of the Bonding and Diffusive Kinetics on the Degree of Acetylation of "Dense Layer" Cellu- lose-Acetate Membranes and on the Concentration of Included Water	23
5) Differential Scanning Calorimetric Measurements (D.S.C.) of the Transitions Characteristic of the "Dense Layer" Materials	26
6) The Influence of NaCl on the Bonding and Diffusive Kinetics of the Included Water in a CA _{7.5} Membrane.....	30
7) The Dependence of the Bonding and Diffusive Kinetics on the Molecular Weight of "Dense Layer" Cellulose- Acetate Membranes	32
8) Initial Investigations of the Effects of Heat Treatment on "Dense Layer" Cellulose-Acetate Desalination Membrane	35
TABLE I: Characteristics of "Dense Layer" Materials and the Amount of the Included Water Used as Samples for N.I.S. Investigations	36
FIGURE 1 through FIGURE 14	37 - 50
REFERENCES.....	51

ABSTRACT

Neutron spectroscopic investigations were initiated to systematically study and determine, at a molecular level, the factors and properties that control the diffusion and bonding of water in "dense skin" cellulose-acetate desalination membranes. Data have been taken both to determine the functional form of the diffusive kinetics that characterizes the transport of H_2O molecules in membranes and then study the influence on the bonding and kinetics of the individual water of: a) extent of membrane hydration, b) number of hydrophilic groups (or the membrane acetylation), c) variations in molecular weight, d) temperature, e) the presence of an included salt (NaCl), and f) heat treatment and compaction and their relationship to the casting process.

The functional form of the diffusive kinetics, characteristic of H_2O in desalination membranes, corresponds to an "activated" or "jump diffusion" type process where H_2O molecules remain bonded at a site for a "residence time" τ_0 ; then break bonds and "jump" a mean-square distance l^2 to another bonding site. H_2O 's can migrate uniformly throughout the membrane matrix by such activated jumps between "hydrophilic sites" which may include combinations of polymeric groups, hydrated ions of an included salt, or "water clusters." In contrast to the water, hydrated ions are confined to diffuse through more open and larger free volume regions of the membrane which are "water-rich." Hence, they travel a longer and more "tortuous path" than H_2O 's; thus, a difference in the diffusion mechanisms for the ions and water governs in large part the flux and salt-rejection properties of such membranes.

The initial investigations have demonstrated that significant observable variations can occur in the characteristic self-diffusion coefficients, residence times, and jump lengths due to the above factors in a) through f). Thus, at low concentrations, little evidence was found for secondary H_2O - H_2O coordinations or the presence of significant clusters of water molecules. The water was primarily distributed in a nearly uniform manner over hydroxyl sites in the amorphous regions of the polymer. The diffusive kinetics were in accord with an activated jump mechanism whereby H_2O 's jump between different hydroxyl sites. While the inelastic frequencies characteristic of the bonding of the water molecules on such hydroxyl sites are in accord with a slightly weaker coordination per H_2O than characteristic of normal water, the residence time (e.g., the average time a water molecule remained bonded) was strongly increased. It was hypothesized that the increase in the residence time could result from a larger separation of consecutive "jump sites" than would be characteristic of normal water. The decrease in the self-diffusion coefficient results in part from the increase in the residence time and, in part, from the presence of less free volume for water in the membrane than would be encountered in the quasi-lattice structure of normal water.

However, as the density of hydrophilic sites and the amount of included water were increased, an increase in the diffusive mobility of the

included water was observed and the molecular frequencies changed in accord with the development of secondary water-water coordinations and then of larger clusters. In addition, it appeared that dispersion in local orderings at O--O distances of such clusters was larger than that which would be characteristic of those in pure water. Indeed, it appeared that such clusters might be considered "broken-down" or "disrupted" relative to normal water at 25°C and could be more characteristic of the behavior found in normal water at higher temperatures. This behavior was attributed to the interaction of such clusters and hydrophilic groups in the immediate vicinity of the polymer, and also, in part, to steric constraints the free volume in the polymer may impose upon their size.

In correspondence, as the concentration of included water increased, a large decrease occurred in the residence time for the activated jumps. The change in diffusive mobility and a strong decrease in the residence time could reflect the weak and disrupted coordinations in such clusters as well as a decrease in the average distance between sites of activated jumps relative to low water concentrations where H₂O molecules primarily jump along hydroxyl groups only.

Both neutron spectroscopy and D.S.C. showed no indication of the formation of hexagonal ice down to -50°C. Indeed, neutron spectra showed that the molecular coordinations of the H₂O's and their corresponding intermolecular vibrations were preserved to -50°C. These results showed that the coordination and dispersion of water molecules throughout the membrane together with the limited free volume were sufficient to inhibit ice formation in these materials. These results emphasize that "membrane-water" is significantly different from normal water. Further, the membrane matrix to a first approximation must be considered as a "solute" with which the included water interacts significantly strongly so as to allow the solution to be supercooled and to inhibit ice formation.

A significant change in the diffusive mobility resulted from the NaCl in correspondence with an increase in the self-diffusion coefficient and a decrease in the residence time relative to the membrane containing only water such that the equilibrium diffusion of water in the membrane had been enhanced by sodium chloride. This increase in diffusive mobility has been tentatively associated with a decrease in the average distance between jump sites due to the presence of the sodium. Thus, if only water is present, a water molecule will diffuse along adjacent OH groups in the amorphous region. When sodium is present, a water molecule may migrate from an OH to an ion and then to another OH group. Hence, the effective jump distance is reduced and the diffusive mobility is increased. The sodium ion may act in this manner as a center for an activated jump even though the average time that a water molecule would be coordinated to it would be small compared to its equivalent residence time on a hydroxyl group.

For cellulose-acetate membranes with a fixed degree of acetylation a decrease in molecular weight caused an increase in the diffusive mobility of the "dense layer" material. The self-diffusion coefficient was observed to increase with the decrease in molecular weight, but no significant change occurred in the residence time, τ_0 , associated with the average period that

an H₂O remains bonded for undergoing an activated jump.

To complement the neutron scattering results, differential scanning calorimetric (D.S.C.) measurements were made to determine the transitions characteristic of the "dense layer" materials. A degree of similarity existed in both the number and types of transitions observed for the samples. In the vicinity of 217°C - 240°C, a first-order transition is observed characteristic of the melting of crystallites. Below this transition in temperature, a second-order glass transition is observed typically in the region between 170°C and 200°C. In general, the above two types of transitions appear common to cellulose-acetate materials. However, their characteristic temperatures and intensities vary, depending upon the material, the degree of acetylation, and the casting procedure. In addition, a second-order glass transition is observed at lower temperatures and strongly depends upon the casting procedures and is associated with regions of larger free volume. The relationship between these transitions and the membrane morphology as well as variations that result from different casting techniques and heat treatment are discussed.

I. INTRODUCTION

During the 1971-1972 contract year, work has been initiated to apply inelastic neutron spectroscopy (N.I.S.) to studies of the bonding and diffusive kinetics of water included in "dense layer" cellulose acetate membranes typical of those used for desalination. Previously, N.I.S. has been applied (1-10) to study the intermolecular frequencies of H₂O molecules in hydration layers of ions or in solvent structure and, simultaneously, of the corresponding diffusion kinetics. The present program represents an extension of such studies to water in cellulose-acetate "dense layer" membranes.

The development of high-flux, low-cost, long-life membranes, the improvement of membrane separation, and the development of new improved materials are fundamentally related to polymer-water, water-water, and water-salt interactions, and to the polymer morphology. These constitute important factors for such materials in determining the flux and salt rejection properties. A better understanding of such phenomena should benefit in designing and optimizing the materials and components used in desalination processes. Nevertheless, an unambiguous identification and description of the transport processes for water molecules in desalination membranes at a molecular level and the forces and ordering for water molecules that underlie and determine such transport processes is lacking. Further, even for a given type of membrane material, such as cellulose-acetate, the history and preparation of the membrane including heat treatment or annealing, swelling, and compaction may strongly affect their resistance to transport and alter the permeability and/or salt rejection of the active layer(11-17). However, again the precise manner by which such changes and alterations affect the molecular transport of water molecules is still far from well understood such that influence can be predicted in a reliable manner.

Specifically, it was the purpose of this initial investigation to provide information on (a) the intermolecular frequencies characteristic of H₂O molecules in membranes and, simultaneously, the functional form and the related parameters that characterize the diffusion of water molecules in such materials; (b) the variation of the above bonding and diffusion properties of H₂O molecules that result from variations in membrane properties including molecular weight, degree of acetylation, compaction, and heat treatments; and (c) direct information at a molecular level that will aid in the determination of specific polymeric properties of the membrane and their correlation with the bonding and transport of water molecules in such materials that would relate to the flux and the salt rejection properties of the materials.

Neutron spectroscopy constitutes a powerful technique with which to study the diffusive kinetics, the various components that contribute to the overall transport process and their relationship to the interactions between the water molecules and membrane materials of interest for

sea water desalination. The relaxation processes of water molecules in such membranes will give rise to broadening of the incident energy distribution (the quasi-elastic component). By studying the shape, the angular, and the temperature dependences of the broadening function, information can be obtained about the microscopic diffusional process of water in membranes and be related to such important quantities as salt rejection and flux.

Neutron scattering techniques have been devised to allow spectra of the neutrons scattered by the water in membranes to be reproducibly and reliably extracted from measured spectra which include contributions both from the water and the membrane. Such spectra provide direct information on

- (a) the intermolecular frequencies (below 900 cm^{-1}) that characterize the bonding and local ordering of H_2O molecules in the membrane
- (b) the functional form of the diffusive kinetics (the related parameters including self-diffusion coefficients and residence times)
- (c) the variations in the bonding and diffusive kinetics of the included water both relative to normal water or to salt solutions that occur as the result of the changes in the diffusion kinetics at a molecular level can be studied as a function of such factors as compaction, heat treatment, degree of acetylation, molecular weight, and the type of membrane material itself.

For these initial investigations, techniques were developed to cast "dense layer" cellulose-acetate materials typical of the "dense" skins of desalination membranes and also suitable samples for N.I.S. measurements. In addition, experimental techniques and computer programs were developed to allow a spectrum characteristic of the included water to be "unfolded" in a reliable and reproducible manner from the measured spectrum which contained contributions both from the water and from the membrane material itself.

The results of our initial measurements have demonstrated that reliable and reproducible neutron spectra, characteristic to water in membranes, can be obtained and can provide direct information at a molecular level on the bonding and diffusive kinetics of the H_2O molecules. Further, both the kinetics and bonding of such waters are observed to differ significantly from those of pure water as a result of polymer-water interactions and the constraints of the polymer in free volume. In addition, measurements to date show that significant variations in the bonding and diffusive kinetics can be observed due to

- a) temperature;
- b) increased membrane hydration and the formation of secondary water-water coordinations and of water clusters which compete with the interactions between hydrophilic polymer groups and water;
- c) variations in the hydroxyl content of the membranes with variations in acetylation of the cellulose-acetate membranes;
- d) interactions between the water and a salt in the membrane; and
- e) molecular weight variations.

Such measurements allow a direct determination at a molecular level on the variations that the above factors produce on the bondings, the diffusive kinetics and associated parameters (including self-diffusion coefficients, residence times, and jump lengths) characteristic of the included water.

In addition to neutron scattering, two other techniques have been used to provide complementary information. Differential scanning calorimetry (D.S.C.) measurements on "as cast" membranes and membranes exposed to water or an aqueous solution provide information on the transitions characteristic of the amorphous or crystalline regions of these materials. Further, such measurements provide information on how such amorphous regions and crystalline regions vary due to casting procedures, due to membrane composition, or due to any morphological changes that may have occurred as the result of included water. In addition, for membranes that have been soaked in aqueous ionic solutions, emission spectroscopy has been used to determine the amount of the salt that has entered the membrane and, hence, to make an estimate of the "effective concentration" of the solution included in the membrane.

II. EXPERIMENTAL

1) Instrumental

The measurements were made using the beryllium-filtered incident beam and a time-of-flight spectrometer described in detail previously (5,18). The solutions were prepared from reagent grade materials and deionized water. The samples were contained in an aluminum sample holder, appropriately shielded so that the neutrons could only be scattered from the membrane. A thin layer of an inert polymer film (2 μ in thickness), plated on the cell and the aluminum windows, afforded protection against corrosion without significantly contributing to background. Measurements have shown that the sample thicknesses used yielded negligible spectral distortions due to multiple scattering. For spectra measured below 0°, the samples were cooled by flowing liquid nitrogen or liquid nitrogen boil-off gas through a channel in the sample holder and the temperature was controlled to $\pm 2^\circ$. Care was taken to prevent condensation on the scattering surface

of the sample. For spectra taken at $+1^\circ$, the sample was cooled by circulating water from an ice bath and was shielded to avoid scattering of neutrons by the coolant.

2) Development of Experimental Techniques and Sample Preparation

To obtain a spectrum of the included water it was necessary to unfold a spectrum characteristic of the hydrogenous polymer from a spectrum characteristic of the wet membrane which would include contributions of neutron scattering from both protonic groups of the membrane as well as from the water. In most previous neutron inelastic scattering studies of included species, the measurements have been confined to investigating the vibrational modes and the diffusive kinetics of hydrogenous molecules in nonhydrogenous substrates or in perdeuterated substrates. In such cases, as the neutron scattering cross section for hydrogen is large relative to that for most other atoms, the spectra so obtained are primarily characteristic of the hydrogenous species and a background subtraction becomes unnecessary.

For membranes containing H_2O , a subtraction of the membrane spectral contribution must be done with care to avoid spurious effects and spectral distortion. Sample holders and sample holder positioning devices were designed and built to insure identical scattering geometries when running the membranes with included water and without included water. The spectrum of the "wet" and "dry" samples was then run under such identical geometries, under constant flux conditions and for an identical number of chopper cycles (e.g., neutron bursts). Further care was exercised to insure that during such runs and from run to run the wet sample had not changed its water content nor had the dry sample picked up moisture. Care was also exercised to insure that both the wet and dry sample materials were identical with regard to area and thickness. The only difference was that one sample contained a specified amount of light water and the other did not. Both the wet and dry samples were sufficiently thin so that their individual spectra would not contain significant contributions from multiple scattering processes and, in particular, the probability of multiple scattering would not be enhanced for the wet sample relative to the dry. Measurements were also made to insure that backgrounds were identical for both sample measurements.

In addition, the possibility was considered that the presence of water in the sample could have changed the membrane morphology and effected the extraction of a reliable water spectrum from the measured spectrum. Thus, spectra of the "as cast" dry membranes were compared to spectra of the same material containing heavy water. As the neutron scattering cross section is larger (by approximately an order of magnitude for scattering from hydrogen compared to deuterium or most other elements), any spectral changes between the "dry" membrane and the membrane containing heavy water or D_2O solution would reflect corresponding changes in the low frequency modes characteristic of the polymer that might occur as a result of swelling or morphological changes due to water. If such changes are observed, the heavy water swollen membrane can be used as a standard "background

spectrum" and subtracted from the spectrum of the membrane containing the equivalent amount of light water to obtain the neutron spectra of the included water.

The casting procedures have been carried out in cooperation with Dr. L.M. Litz (Union Carbide Research Institute, Tarrytown, New York) and members of his Membrane Process Group (currently under contract with the Membrane Division, Engineering and Development, Office of Saline Water, U.S. Department of the Interior) to ensure that the obtained materials are reasonable representations of commercial membranes used for desalination. It is, however, to be emphasized that in certain cases (e.g., the material cast from E-320, as discussed below) such "dense layer" materials have been chosen specifically to provide information on changes in water transport in the materials as a function of variation of the membrane composition and morphology even though their flux and salt rejection properties would be below commercially acceptable ratings. Neutron scattering measurements were made on the included water and on a sodium chloride solution in a $CA_{2.5}$ membrane cast from E-398-10 cellulose acetate having a 39.8% acetyl content. Spectra, as a function of scattering angle, have been obtained for (a) a sample of this material containing 10 wt.% water, (b) a sample of this material containing 5 wt.% water, and (c) a sample of this material that has been exposed to a 4.6 m (12 water molecules per ion pair) NaCl solution. Eastman cellulose-acetate E-398-10 powder was initially dissolved in acetone to make a 20 wt.% solution. The thick solution was poured on a flat glass plate and a scribe was used to form a thin layer. This layer was then allowed to dry in air and further vacuum dried at room temperature for 24 hours in a desiccator. The $CA_{2.5}$ "dense layer" material so produced was soaked in deionized water for 24 hours at room temperature. It was determined that the total water pick-up was 10 wt.%.

Measurements show that the sample soaked in the sodium chloride solution had gained approximately 10 wt.%. Emission spectroscopic measurements have been used to estimate the amount of sodium chloride picked up. These combined results indicate that the "effective concentration" of the sodium chloride solution in the membrane will be approximately 1.5 m (approximately 30 H_2O 's per ion pair). Thus, a comparison of the spectra of included water in this material relative to the sample that has picked up 10 wt.% pure water provides information on the influence on the bonding and diffusive kinetics of H_2O molecules caused by the presence in the membrane of one NaCl per 30 H_2O 's.

In order to determine the influence on the transport of water, molecules in "dense layer" cellulose-acetate materials associated with different water concentrations, a "dense layer" $CA_{1.7}$ membrane was cast from Eastman-320 cellulose acetate (32% acetyl content). It had approximately three times the number of OH groups as the above $CA_{2.5}$ membrane cast from E-398-10. This membrane was prepared from a DMSO solution, and the casting procedures were effectively identical to those described above. Upon being soaked for 24 hours, it picked up approximately 24 wt.% (in accord with reported data that the water adsorbed approximately linearly for the hydroxyl content of the material).

A "dense layer" $CA_{2.08}$ membrane was cast from Eastman A-432-130B in 12 wt.% methylene chloride solution following the procedures used to cast the $CA_{2.5}$ membranes. The heat treatment on the E-398-10 membranes was done by dipping the membranes in hot water at a specific temperature (as indicated in the data) for 5 minutes and then immediately transferring the membrane to a room temperature water bath.

The sample used for compaction study, due to the size and geometry of the sample, cannot feasibly reproduce the dynamic compaction conditions. Rather, the present measurement is to study the effect on the included water by applying hydraulic pressure on the membranes which may affect the membrane structure before true equilibrium is attained. The "compacted" sample was prepared by soaking the cast E-398-10 membrane in a tank of water and applying 1500 lb/in² pressure for two weeks.

5) Analysis of Data

The spectra were corrected for background, for counter efficiency, and for chopper transmission. The background corrections were made by a channel-by-channel subtraction of the spectra obtained for the empty sample holder, and were found to be predominantly a flat component upon which was superimposed a weaker broad distribution, centering at about channel 146. This latter component, which varied with rotor speed, is ascribed to the 180° burst. Statistical uncertainties were calculated from the total number of background counts and the number of observed counts per channel. Further, the reproducibility and reliability of spectral features were checked by comparisons of spectra remeasured at different times with new solutions; comparisons of data collected from four independent counter banks, electronics, and memory banks from the time-of-flight analyzer; and a comparison with background spectra for the empty cell to show that no spectral features or maxima arose from the sample holder or the aluminum window. The solid curves in Figures to were averaged through the data points with regard to statistical uncertainties. The half-width at half-maximum, Γ , for the Lorentzian function associated with a diffusively broadened incident energy distribution was determined in a manner described in detail previously (5). Specifically, Γ 's were selected by comparing the observed quasi-elastic component with the measured incident-energy distribution which had been further broadened by a series of Lorentzian functions of varying half-widths at half-maxima.

III. RESULTS AND DISCUSSION

The results of N.I.S. and D.S.C. measurements made during the 1971-1972 measurements will be discussed below and considered together with results of other techniques and current theory. Thus, prior to considering the results of this investigation, a number of more recent results and theories pertinent to the bonding and transport of H₂O and ions in dense layer materials will be reviewed.

1) Review of Background Information

A. The Diffusion Process for Water in Membranes

A quantitative understanding of the mechanism of water transport in membranes, its specific relationship to the type of membrane, to the nature of the membrane-water interaction, and to the preparation and treatment of the material can provide important fundamental information for the development of high-flux, low-cost, long-life membranes. Many materials, both polymeric and inorganic, have been investigated for their potential as reverse osmosis membranes for desalination purposes(11,19-26).

The development of high-flux, low-cost, long-life membranes and the improvement of membrane separation and the development of new improved materials are fundamentally related to the polymer, water, or membrane interactions which, for such materials, are important factors in determining the transport processes of water molecules. A better understanding of such phenomena could benefit designers optimizing the materials and components used in desalination processes. However, an unambiguous identification and description of the transport processes for water molecules in desalination membranes at a molecular level and the forces and ordering for water molecules that underlie and determine such transport processes is lacking, despite the large number of polymeric and copolymeric membranes as well as such materials as porous glasses and graphitic oxides that have been investigated. In addition, even for a given type of membrane material, such as cellulose acetate, the history and preparation of the membrane including heat treatment or annealing, swelling, and compaction may strongly affect their resistance to transport and alter the permeability and/or salt rejection of the active layer. However, again the precise manner by which such changes and alterations affect the molecular transport of water molecules is not well understood.

The manner in which the partial separation of the solution components under reverse osmosis conditions is achieved has remained the subject of controversy(27). It is clear that for "dense skin" cellulose-acetate membranes the permeation coefficients, the salt rejection, and the water fluxes intimately depend on the fundamental nature of the molecular mechanism or mechanisms which govern the diffusive transport of salt and of water molecules. The relationship of such transport properties to the membrane morphology and composition are in turn governed by the interactions between the individual components and the membranes. This is particularly true for "dense layered" materials which are not strongly swollen to an extent that appreciable hydrodynamic or bulk-flow of water and/or salt solution can occur. The situation becomes further

complex when the possibility of mutual interactions between the three components: the membrane, the included salt, and the included water are considered. Such mutual interactions may in turn influence the bonding and the nature of the diffusive transport of each included component in a significant but poorly understood manner.

The nature of the salt rejecting layer has been the subject of numerous discussions by investigators who have studied the Loeb type membranes. In a general sense, there are two depictions or two classes of models of what the surface is like (21, 26, 27, 28). In one case it has been argued that the "dense layer" is microporous having pores typically of 6 to 10 Å in size (28), which is sensitive to differences in size and shape of permeant molecules. Indeed, Osterhoudt has argued that the surface of desalination membranes based on cellulose acetate are highly selective as to the molecular size and shape of uncharged permeances and that this selectivity is greater the more the salt rejection of the membrane. Bean and DeSorbo (21) have recently argued (from studies of salt rejection in the cellulose acetate as a function of pressure) that a rough agreement between theory and experiment can be obtained upon assuming the existence of pore sizes in the range of 10-20 Å. They conclude that a model, assuming the salt rejection by pores, cannot be excluded in explaining the properties of cellulose acetate. However, direct independent physical evidence for the existence of such pores appears lacking. Indeed, in many cases the large number of parameters associated with such pore models is sufficiently great so that there is very little that they cannot "explain" (15). Further, the nature of the pores themselves has been the subject of discussions. Thus, it has been argued that there may be two types of pores -- a larger unrestricted type pore through which the permeates can diffuse, and a "restricted" type pore which requires a degree of pressure activation to effectively open it and allow the permeant to pass. Also, as smaller pore sizes are considered, the conceptual distinction between a "pore" and amorphous region of the polymeric membrane becomes abstract and poorly defined.

An alternative picture of the active or "dense skin" surface has been presented by a number of authors. Thus, it has been argued that both the salt and the water flux through the membrane material result from the fact that the permeants first dissolve in a polymeric material and then diffuse through it. In such models, the difference in the mechanisms for diffusion of the two components together with the differences in their respective concentrations in the membrane primarily are believed to account for both the salt rejection rate and the flux properties of the material. Indeed, combinations of these models have been also proposed in which, at low hydration, the water and salt fluxes are due primarily to diffusion processes and are to the first approximation uncoupled (12, 13, 14, 29). In contrast, at higher hydrations, coupling between the two fluxes results and "bulk flow" becomes important.

Many features of proposed theories can be tested by and compared with results of N.I.S. measurements. Thus, Reid (30), and Hoffman et al (29) have suggested that the hydroxyl group in cellulose-acetate membranes

are essential for the selective diffusion of water. Water molecules undergo an activated or "jump" diffusion process in amorphous regions of the polymer which involves the breaking of bonds between H_2O and hydroxyl groups. Thus, as noted by Yasuda, LaMaze and Ikenberry (31) that (at least at lower membrane hydrations) the "membrane-phase is uniformly solvated by the water present." Then, as suggested by Hoffman et al(29) such primary H_2O 's might be expected to diffuse by jumping from chain to chain when hydrophilic groups are in close proximity. In turn, this implies that the density and strength of hydrophilic sites play a crucial role in determining the flux characteristic of such "dense layer" materials.

However, a number of considerations serve to make such a model more complex. Thus, Rosenbaum et al(16) have noted that, for C.A. membranes with low hydroxyl content, the strong dependence of the self-diffusion coefficient for water on the density of hydroxyl groups present appears to be reduced. Thus, it appears possible that functional groups in polymer chains, other than hydroxyl groups, may play a role as "activation sites." Further, while the free volume, on the average, may be sufficiently large to sterically permit the passage of H_2O undergoing jump diffusion, it may still strongly limit the size of any water clusters present and impose geometric constraints that decrease the self-diffusion coefficients. In addition, it appears that the equilibrium water content of such membranes increases with increasing hydroxyl content. Hence, the probabilities both of forming secondary water and/or clusters as well as swelling the polymer and increasing the free volume are enhanced at higher hydrations. In turn, this implies that the influence of clusters and secondary water-water coordinations and variations in free volume on the jump diffusion of individual H_2O 's must be considered. At such higher hydration, a "capillary" or "bulk" flow of water may occur in addition to diffusion as argued by Yasuda et al(13,14,31). Thus, the type and number of hydrophilic groups may strongly determine the flux behavior of the membrane by both effecting the activation energies and jump lengths for individual H_2O 's but also determine the extent of secondary water coordinations and clusters which can in turn affect the diffusion process.

Thus, Hoffman, Model and Fleming(22) have proposed a model for the diffusional water in hydrophilic membranes in terms of two transport water mechanisms. Primary, H-bonded water can diffuse along hydrophilic sites, and salt ions and secondary H_2O 's can diffuse between "clusters" in narrow, capillary-like passages. Thus, as noted by Huang and Jarvis(32), as amorphous regions in the hydrophilic polymer become swollen at high water concentrations, the polymer chain segments may become more mobile, and thus a decrease may occur in energy of the diffusive transport through the membrane. These effects are reflected in increasing salt permeation rates and decreasing separation as the water content is increased. Thus, at high water concentrations, the water may have, in essence, a plasticizing effect on the polymer membrane. A similar conclusion has been reached by Vieth, Douglas, and Bloch(33) who suggest the following type of correlation. Highly hydrophilic polymers, in general, have high water contents, high water transport, but low salt rejection. This appears to be the result of an expansion of the membrane

by swelling with the solvent which creates more favorable diffusive pathways for water and ions. Strongly hydrophobic membranes would be characterized by medium to high clusters and low diffusivities. The authors associate large clusters of water with excess volume microcavities in the polymer structure. However, unlike the hydrophilic polymers, this probability of diffusive pathways between such clusters would be low. These authors argue that cellulose acetate, under certain conditions, may correspond to an intermediate case with low cluster sizes and intermediate diffusivities. Thus, the degree of water clustering would be sufficiently low so that where large clusters would not exist and the polymer would not be excessively swollen, still the diffusivities and connecting paths would have acceptable values.

Recently, Peterlin and Yasuda (34) have argued that the diffusion coefficient for salt through a polymer membrane can be described as a function of the membrane hydration, of the size of the solute, and of the probability of finding pores equal to or larger than this size. On the other hand, they note that the diffusivity of water in a swollen membrane is more complicated as the water may interact strongly with hydrophilic polymers and that the permeability of water under pressure can deviate progressively with increasing hydration from that expected for a diffusive permeability. Thus, they suggest the water in a strongly swollen membrane may pass through partially by a process involving bulk flow which in turn reduces the salt rejection and increases the flux of both water and ions. They also argue that the interaction between water and the polymer seems to be a predominant factor influencing the water flux and the salt rejection characteristics. These authors also investigated the N.M.R. spectrum for water in membranes. They found, indeed, as expected that the N.M.R. signal was broader for water in the membrane phase than for free water due to restriction of the molecular motion. However, they also noted that, while such a broad water signal was observed for all the polymers investigated, at higher activities of water a number of polymers showed a doublet which, while not a simple superposition of a pure water line on a signal of included water, might arise from preferred orientation of the H_2O 's in the polymer. Further, they noted that the temperature dependence of the N.M.R. lines of the water in the polymer was significantly different from that of pure water and the N.M.R. signal did not change appreciably down to $-90^\circ C$ where an abrupt broadening occurred. Thus, cooling did not affect the absorbed water and its molecular motion until temperatures well below 0° were reached.

Recently, Yasuda and coworkers(13,14), have analyzed the relationship in reverse osmosis membranes between salt rejection and water flux on the basis of movement of water through the polymer. They note that, under applied pressure, both molecular diffusion and bulk flow can occur in polymer membranes in a manner dependent both upon the water content and the degree of swelling of the material. They also argue that the interaction between the solute flux and the water flux can be appreciable. Thus, as long as the water moves by diffusion it is unlikely

that the coupling of water and solute flux will occur; but, when water moves by bulk flow, the coupling may be significant and the salt rejection of the membrane may drop. In the lower hydration region, they found that water permeates by diffusion even under an applied hydraulic pressure; while, in the higher hydration region, water moves partially by bulk flow under an applied pressure gradient but moves only by diffusion in the absence of pressure gradient. In a homogeneous membrane they conceive of the water-filled space through which transport of permeates can occur as fluctuating pores or channels in the polymer matrix which are not fixed either in size or location. As a consequence of the plasticizing effect of water in swollen membranes, macromolecules in the water-swollen polymer may exhibit a high degree of mobility so that the size and shapes of the pores or channels may continuously change. Therefore, at a certain point within the membrane at a fixed time the geometry of the polymer segments may be such that the water movement is characterized by diffusion. Water may move more and more by flow when this portion of the membrane structure changes to a more loose geometric arrangement at some later moment. Therefore, in order to have high salt rejection rate and high water flux, the membrane must have a maximum amount of water distributed evenly throughout the membrane without the formation of large clusters and/or aggregates of water. However, polymer systems are not expected to be homogeneous at a microscopic level. Regions of widely varying degrees of free volume including crystallites, spherulites and amorphous fractions may co-exist and be distributed throughout a polymer volume. Thus, Yasuda and Tamaze (13) have estimated that even in cellulose-acetate membranes intersegmental spaces of at least 30-40 Å may be able to exist. It is of interest to note that cavities of such a size, if they did not modify the structure through surface interactions, would be sterically capable of holding clusters which might approach those typical of normal water. As recent x-ray diffraction data have shown, all 0--0 correlation in normal water is lost only at radii larger than 20 Å.

In addition to the above results, Yasuda and his coworkers (13,14) have described the microscopic diffusional water in the membrane in terms of thermally activated jumps of individual water molecules for which the self-diffusion coefficient, D , is given by

$$D = v \exp[-V^*/V_f^0] \exp[-E/kT] \quad \text{Eq. (1)}$$

where

$$v = d^2 (kT/h); \quad \text{Eq. (2)}$$

d is the jump distance; V^* is a characteristic volume parameter describing diffusion of the permeant molecules in the membrane (in essence proportional to the sweeping volume); and V_f^0 is the total free volume in unit volume of the membrane; E is the activation energy for the diffusion process. The authors note that the exponential term involving the activation energy can be considered as characteristic of the water molecules describing a thermal translational jump, while the exponential term involving

the free volume is characteristic of the membrane. Further, the exponential term involving the free volume of the membrane was included by the authors in accord with concepts developed by Cohen and Turnbull(35). Physically, it represents the probability of a molecule finding a hole to which it can jump from a given location and is therefore strongly dependent on the morphology of the polymer and of the regions of included water in the polymer. Further, the authors assume that V_f^0 , the total free volume of the membrane, is composed of additive contributions both from free volume characteristic of the polymer morphology and a free volume characteristic of water clusters in the membrane, $V_{f_1}^0$. The relative amounts of each type of free volume are related to the volume fraction (H) of the water in the membrane or of the polymer. The authors further assume that at high water concentrations the activation energy for water in a membrane may be closely similar to that for pure water in which case Equation (1) can be rewritten in terms of the self-diffusion coefficient for pure water, D_0 , as the following:

$$D = D_0 \exp[-V^*(1/V_f^0 - 1/V_{f_1}^0)] \quad \text{Eq. (5)}$$

It is of interest to note that to the extent that this approximation is valid, the D for water in membranes would be suppressed relative to the D_0 for normal water by the geometric free volume factor. Further, it should be noted that this equation is of interest in comparing the functional form of parameters of the diffusive kinetics obtained by neutron inelastic scattering for those obtained previously for water and ionic solutions. One might expect in this approximation that the residence time, τ_0 , which depends primarily upon the activation energy would remain similar to that for water, while the observed self-diffusion coefficient would be strongly suppressed by the free volume exponential factor in Equation (3). By a comparison of the functional dependence of Equation (3) for a series of membranes for which the ratio of the volume percent for water and polymer are known, the authors conclude that self-diffusion coefficient in the range of hydration from $H = 1$ to 0.1 can be, indeed, described by Equation (5) which was derived both on the basis of free volume concept of diffusion in membranes and on the assumption of additivity of free volume of the polymer membrane and hydration water. As will be discussed in detail below, the initial neutron scattering results on a cellulose-2.5 acetate membrane containing approximately one H_2O per OH group (assuming the uniform distribution of waters) show features (detailed below) that are partially in accord with the above authors' findings. However, they cast doubt on the assumption that, at lower hydrations of the membrane, the average activation energy involved in individual H_2O molecules is similar to that for pure water. Thus, at such lower hydrations, $OH \cdots H_2O$ bonds would be expected to predominate relative to direct $H_2O \cdots H_2O$ coordinations characteristic of "clusters" in swollen areas of the membranes, and the former might involve a significantly different hydrogen bonding strength than that characteristic of pure water. Such differences would then show up in a pronounced manner both in the inelastic frequencies and the values of τ_0 , the residence time, which depends upon the activation energy. In addition, the self-diffusion

coefficient would be strongly suppressed relative to normal water by just the geometrical free volume factor, discussed by the authors above.

It has been argued by Rosenbaum and Skeins(15), by Reid and coworkers(30), by Yasuda and coworkers(13,14,36) and by Hoffman and coworkers(29) that the amount of salt in a membrane is closely connected to the membrane hydration on the dissolved salt in the polymeric matrix which is solvated and is ionized to a similar degree to that in solution. However, this should not be taken to indicate that the concentration of salt in membrane water and the degree of hydration of the ions would be equivalent to a solution. Thus, while ions in a membrane may be solvated to an extent to shield them from direct interactions with the cellulose-acetate polymer, as argued by Yasuda et al(31), water-polymer interactions and the extent of local free volume available for hydrated ions may alter the salt hydration relative to a pure salt solution. It has been suggested that ions in membranes will primarily be confined to and diffuse between more open water-rich regions in a membrane in which there is enough H₂O so that multiple ion-water contacts can occur. Thus, as suggested by Hoffman(22), "hydrated ions would travel a longer and more tortuous path" than H₂O molecules in traversing the membrane and, hence, effectively diffuse more slowly. Further, as noted by Yasuda et al(13,14) at high hydrations where appreciable swelling and increase in free volume can occur, the salt flux can "couple to the water flux and a bulk or macroscopic transport of salt may occur." Highly hydrophilic polymers in general are thought to have higher water contents and high water transport but, as noted above, a relatively low salt rejection. The latter property results apparently from the result of an expansion of the membrane by swelling with the solvent which, in turn, creates more favorable diffusive pathways through the film for water and ions.

Thus, it has been argued by Michaels et al(12), by Yasuda and Schwindler(36), by Rosenbaum et al(15,16), and by Hoffman et al(29) that essentially the desalination efficiency of reverse osmosis membranes is due to such differences in the diffusion mechanics for water and for hydrated ions that occur as a result of the different polymer-water and ion-water interactions. However, at lower hydrations, any degree of coupling between the salt flux and the water flux has generally been neglected. Our initial N.I.S. investigation of the effect of NaCl on the bonding and diffusive kinetics of the water in "dense layer" membranes (as detailed below) casts some doubt on this assumption. At lower membrane hydrations (e.g., especially ≤ 10 wt.%), measurements showed that substantial changes occurred as the result of included NaCl in the diffusive mobility of the included H₂O molecules.

B. Effects of Temperature

Only a limited number of measurements at a molecular level for the effects of temperature on H₂O in desalination membranes is available. Thus, Peterlin and Yasuda(34) have made N.M.R. measurements on the temperature dependences of the included water. These authors have noted a broader N.M.R. signal for water in polymers typical of those used for desalination membranes. Indeed, not only was the signal of water in such

polymers broadened relative to normal water, but certain polymers showed a doublet which the above authors argued might occur due to the fact that certain of the water molecules or certain motions of such water molecules had preferred orientation. Further, these authors note that the N.M.R. signal of such water in cellulose acetate did not show any abrupt or appreciable changes down from -90°C where an abrupt broadening then occurred. This, they interpreted as indicating that water exists in such a manner in such membranes that freezing does not occur and the molecular motion of the absorbed water is not abruptly influenced until the temperature dropped far below 0°C . Such behavior is reminiscent of that observed and previously studied^(3,4) in concentrated ionic solutions which, upon supercooling, lead to the formation of viscous, supercooled liquids and, at lower temperatures, glasses having a "frozen-in" order similar to that of the solution structure.

C. Variations in Molecular Weight

F.S. Model et al.^(37) have investigated the influence of molecular weight on reverse osmosis desalination membranes. These authors determined the changes in water flux for a 90% salt rejection that occurred due to variations in molecular weight. While the scattering of data points was large, they did appear to find a trend that indicated that the water flux increased nearly linearly with decreasing molecular range, typically in the range of 20,000 and 70,000. This trend is in keeping with the above preliminary neutron scattering measurements on the effects of molecular weight. Further, the above authors suggested that there is an optimum value of molecular weight which would be in the vicinity of 40,000 for cellulose-acetate desalination membranes.

2) Neutron Spectra of Water in "Dense Layer" Membrane

In Figures 1 and 2, the inelastic spectra obtained by the above subtraction techniques for the included water in a cellulose-2.5 acetate "dense layer" are compared with the corresponding spectra for normal water at 25°C . In the inelastic spectrum of normal water in the vicinity of 400 cm^{-1} the broad intense maximum corresponds to the librational modes of H_2O molecules characteristic of the short-range ordering and bonding of the liquid. Recent neutron inelastic scattering measurements by Safford et al.^(1) have shown that this broad maximum consists of three partially resolved maxima at approximately 460 , 605 and 870 cm^{-1} . Indeed, these values are in agreement with the Raman spectra of Walrafen who deduced the existence of peaks at 450 , 550 , and 722 cm^{-1} . The existence of these maxima has been more recently further confirmed by the work of Day and Sinclair⁽³⁸⁾ using neutron down-scattering experiments with their corresponding peaks at approximately 480 , 645 , and 870 cm^{-1} . These three maxima are associated with the librational rocking, twisting and wagging modes of bonded H_2O molecules in the water structure, and have been associated in the work of the Raman results of Walrafen,⁽³⁹⁾ and of Terhune, Savage and Maker^(40) with a four-coordinated species having C_{2v} symmetry which is progressively broken down with increasing temperature. A number of weaker modes appears at lower frequencies (typically, below 300 cm^{-1}) (e.g., between channels 60 and 140 in the region expected in which hydrogen-bond stretching and bending vibrations would be expected). Again, the

accord between the neutron results and the Raman results are good; although in the absence of selection rules, neutron measurements show additional maxima.

In comparison with the above characteristics of the water spectrum at 25°, the following observed features of the neutron spectra (Figures 1 and 2) for the water in the membrane should be noted.

(a) A broad maximum again appears in the vicinity of 450 cm^{-1} (e.g., channel 49) where librational modes characteristic of normal water typically occur. However, this maximum appears to be the superposition of a larger number of sharper and better resolved components. This multiplicity of components suggests the existence of more than one type of coordination of water molecules in the cellulose acetate. Further, the narrow widths and, hence, better resolution of these vibrational maxima suggest that these coordinations are more unique with regard to distortion and variations in O--O distances than are the four-coordinated species characteristic of normal water.

In addition, as shown in Figure 2, as the concentration of water in the membrane is reduced by about 50%, certain of the maxima in the torsional region appear to become sharper and better defined. This suggests that a broader spectral contribution present at the higher concentration has reduced, thus, leaving the remaining modes unshifted but better resolved and defined. This concentration behavior is again in keeping with the presence of more than one type of coordination for the water in the membrane material. At the lower concentration where the spectral features are sharpest, it could be expected that the majority of H_2O 's would be coordinated directly to OH groups in the amorphous regions of the membrane. Such coordinations could have less dispersion in O--O distances and bond strengths than in pure water and, hence, give rise to sharper and more unique spectral features. As the concentration of water in the membrane is increased, the probability of forming secondary H_2O - H_2O coordinations and/or "clusters" would be enhanced which, in analogy to normal water, would involve a broader distribution of O---O distances and bond strengths and, hence, would give rise to broader spectral components. It is, of course, also possible that the broadening with increasing concentration occurs as the result of the perturbation of the more unique OH- H_2O coordinations and their frequencies by the formation of secondary H_2O -- H_2O coordinations.

(b) The area of the quasi-elastic maximum (e.g., the rise in intensity at channel 165 - 170, followed by a gradual decrease at higher channels) is smaller relative to the inelastic intensity than that characteristic of normal water. If the area of such a maximum is associated with a Debye-Waller exponential, its decrease in intensity or area would be associated with a larger average vibrational amplitude than for water molecules in normal water.

(c) In Figure 3, the Lorentzian half-width at half-maximum, Γ , of the diffusively broadened quasi-elastic component is shown as a function of the momentum transfer squared (K^2). The corresponding curves for normal water at 1°C and at 25°C are also shown. It is seen that the curve for the included water lies well below that for normal water. Its slope at the

origin would be in proportion to $\sqrt{DK^2}$ and, thus, the lower slope implies a reduction in the self-diffusion coefficient relative to normal water. As noted above, such a reduction in the self-diffusion coefficient could be in accord with the argument of Yasuda et al, and could reflect in part the free volume constraints on diffusion as given in Equation (1). More qualitatively, in contrast to normal water, the self-diffusion of individual H_2O 's in the membrane would be reduced by the stronger restraints resulting from free volume restrictions of the polymer. Not only must the probability that an H_2O breaks a bond and undergoes an activated jump be considered but the probability that a "hole" exists into which such a water molecule can pass must also be considered.

At higher K^2 values, the curve of Γ for the included water is observed to closely approach a nearly constant value as expected for a delayed or jump diffusion behavior. In contrast, for pure water at $25^\circ C$ while the curve shows a similar shape, its temperature behavior has been shown not to be (1) in accord with a simple delayed diffusion behavior, and at this temperature, free particle motions may strongly contribute to the observed diffusive behavior. It should be emphasized that recent neutron scattering studies of water and ionic solutions support the recent contentions of Rahman et al (41) that water at 25° cannot be characterized by a simple jump diffusion process as was suggested by earlier neutron scattering measurements. However, studies of the dependence of Γ vs. K^2 for pure water, as a function of temperature (1), show that, in an interval of temperature between $1^\circ C$ and approximately $15^\circ C$, a jump diffusion approximation is capable of counting both the observed shape of Γ vs. K^2 , its observed temperature dependence, and of yielding values of D and τ_0 in agreement with those obtained by other techniques for water.

The Γ vs. K^2 curves for the included water, as noted above, lie well below the corresponding curve for water at 25° and also below a similar curve for water at $1^\circ C$, at which temperature a jump diffusion model is valid. The fact that this curve also lies low at high K^2 values implies an average τ_0 strongly increased relative to that characteristic of normal water even at $1^\circ C$. As the amount of water is further reduced (Figure 2), an additional narrowing of the quasi-elastic maximum occurs, in keeping with an additional reduction in D and an increase in τ_0 . A more quantitative estimate of the changes in these parameters must await complete measurements as a function of angle at the lower water concentration. As discussed below, these changes in τ_0 and D can be correlated with the progression in decreasing concentration toward a wider separation of the sites between which the H_2O 's can jump. Thus, at lower concentrations, where H_2O 's would be coordinated primarily to OH groups of the polymer, the average inter-site distance could be larger than at higher concentrations where the presence of secondary H_2O - H_2O coordinations and/or aggregates of H_2O 's could yield shorter distances between jumps.

As seen in the spectra of Figures 1 and 2, real and significant differences relative to water occur both in the inelastic frequencies and in the diffusive broadening of the quasi-elastic maxima for the included water in a "dense" membrane material. Any interpretation of the above data must simultaneously account for (1) the multiplicity of maxima in the torsional region and their enhanced resolution and definition relative to water; (2) the fact that with decreasing water content of the sample, these maxima appear to sharpen and become better defined; (3) a smaller area for the quasi-elastic maximum than is found in the spectrum for normal water, implying a larger average vibrational amplitude; (4) a large decrease in D , the self-diffusion coefficient, and an increase in τ_0 as the concentration for the included water is reduced; (5) the existence of large amorphous regions have high segmental mobility even at 25°C; and (6) D.S.C. observations which show that for the 10% water content ice formation does not occur down to -60°C.

The following model appears capable of explaining the spectral features and results to date. However, in view of the preliminary nature of the data, this model as yet must be considered as tentative. At the lower concentration it would be assumed, as noted above, that the majority of the H_2O molecules present are bonded directly to OH groups randomly distributed in the large amorphous regions of the polymer and few, if any, secondary H_2O-H_2O coordinations are present. If it is further assumed that the interaction between a given OH group and a water molecule is primarily determined by the local segmental ordering of the polymer and only secondarily perturbed by the long-range intramolecular chain ordering, then the OH...O distances and bond strengths may be nearly equivalent, and the sharpness and definition of the corresponding torsional modes of the OH...O molecules can be understood relative to those observed in the spectrum of pure water where a wider variety of distances and bond strengths may be present at 25°C. In order to both explain that these torsional components appear shifted down in frequency systematically by approximately 40-50 cm^{-1} relative to those in water and, simultaneously, the lower area of the quasi-elastic peak and, hence, larger vibrational amplitude, it appears necessary to assume a slightly weaker coordination for such H_2O 's than characterize the H_2O-H_2O coordinations in pure water. At first, such an assumption would appear inconsistent with the much lower value of the self-diffusion coefficient and increased value of τ_0 for the included water in the membrane relative to normal water. However, two factors must be considered in this regard -- first, the much lower value of the self-diffusion coefficient, D , relative to the characteristic value for normal water at 25°C, could result from the influence of free volume on the self-diffusion coefficient (see Equation (1)), as suggested by Yasuda et al.(13,14). Thus, while the local coordination of OH groups to polymer segments strongly determines the frequencies and bondings of water molecules coordinated to such polymer OH groups, longer range polymer morphology and the associated free volume would strongly control the self-diffusion coefficient. It would at first appear that the larger value of τ_0 relative to water would imply a higher activation energy and, hence, stronger bonding for the H_2O 's coordinated to the OH groups which would conflict with the above assumptions necessary to explain the inelastic frequencies and quasi-elastic areas of a weaker bonding than in normal water. However, such need not be the case if it is assumed that the average distance between bonded sites for water molecules coordinated to hydroxyl groups of the polymer is substantially larger than the dis-

tance between sites in normal water. Samoilov(42) has presented detailed arguments to show that, when considering activated jumps between two potential minima separated by a barrier, both the depth of the potentials as well as their spacing are important in determining the "effective activation energy" for the jump. For example, if two such wells were infinitely separated, the removal of an H_2O molecule from a well would correspond to an "evaporation process" and require a larger energy than that required to penetrate the barrier between two potentials which are much more closely spaced. To a first approximation, as the distance between two potential minima is decreased (assuming constant potential depths), the height of the barrier separating them is reduced. Thus, as Samoilov points out, the change in the residence time for a water molecule in an ionic solution relative to pure water does not depend alone on the total value of the interaction energy between an ion and a water molecule or between two water molecules but also upon the distances separating the potential minima and the relative shapes of the minima. In essence, it requires more energy to "evaporate" the H_2O molecule from water completely than to simply break a bond and activate a jump within the water structure.

In terms of the present data, if it is assumed that the potential wells corresponding to two successive bonding sites of H_2O molecules on hydroxyl groups are separated on the average more widely than would be the corresponding sites in pure water, a significant decrease in the jump frequency and, hence, increase in the residence time, τ_0 , could be reproduced, in keeping with the above observations. As the concentration of the included water is increased, secondary water coordinations and/or clusters may form. As noted above, such "clusters" could perturb and broaden the sharper frequencies characteristic of the lower concentration and, hence, account for the concentration behavior observed in the inelastic region. Further, they could decrease the average distance between bonded sites and, hence, decrease the value of τ_0 and increase the value of the self-diffusion coefficient. In principle, if it were possible to increase the hydration of the membrane beyond 10% by weight, one might expect the values of D and τ_0 to approach those characteristic of normal water in accord with the arguments of Yasuda et al(13,14). It would appear that the higher concentration cooling point is reached so that secondary H_2O 's may find it energetically favorable to form ice crystallites rather than to remain coordinated to the polymer. However, this would occur at a lower temperature rather than at that for normal water.

3.) Effects of Temperature on the Bonding of H₂O Molecules in "Dense Layer" Materials

In Figure 4, the neutron spectra characteristic of the 10 wt.% water included in a CA_{2.5} "dense layer" membrane at 25°C, -20°C, and -50°C are compared with spectra for water at 25°C and for hexagonal ice. In the interpretation of these data, the following features should be noted and compared:

- a) D.S.C. traces showed no recrystallization maxima or melting maxima (near 0°C) that would indicate the presence of crystalline ice in the water-saturated CA_{2.5} membrane warmed from -60°C.
- b) The neutron spectra at -10°C and -50°C for the "included" water, are significantly different from those characteristic of the spectra of hexagonal ice (see Figure 4). Thus, the sharp, well-defined torsional maxima at 560 cm⁻¹ (5) and the broad acoustical maximum at 49 cm⁻¹ associated with hexagonal ice are both absent. In contrast, reference to the spectra for the included water at -10°C shows torsional maxima at 522, 415, and 351 which are nearly identical to those observed in the spectra at 25°C (for a CA_{2.5} membrane containing 10 and 5 wt.% water) and they are different to the torsional maxima observed for ice.
- c) With decreasing temperature, these torsional maxima maintain their frequencies and sharpen (compared to the spectra for 10 wt.% water in a membrane at -10°C and at +25°C in Figure 4). This sharpening is similar and in the same direction to that seen to occur as the water content in the CA_{2.5} membrane is decreased from 10 to 5 wt.%. Such a behavior has been associated above to a majority of the H₂O molecules being coordinated in a similar and unique manner to polymer hydroxyl groups at the lower concentration, and the number of secondary H₂O-H₂O coordinations and/or clusters is reduced with decreasing water concentration.
- d) With decreasing temperature, the higher frequency maxima reduce in relative intensity in accord with a Boltzmann thermal population factor.
- e) As the temperature is reduced, there is a strong increase in intensity of the quasi-elastic component relative to the inelastic portion of the spectra in correspondence to a rapid reduction in the average vibrational amplitudes of the water molecules.

- f) While neither the -10°C or -50°C spectra show evidence for ice, variations in the torsional peaks are observed between these two spectra. Thus, maxima at 351 are observed in both these spectra and in the room temperature spectra, as shown in Figure 1. The maxima at 522 and 415 (observed in room temperature spectra) initially sharpen and improve their definition as the temperature is reduced. However, at -50°C they appear to coalesce to a single maximum. Such behavior indicates either changes in the local ordering associated with the torsional maxima or the onset of spectral contributions from secondary water coordinations and/or "clusters" which, while different from ice, are also different than pure water and the H_2O molecules coordinated to polymer hydroxyl groups.

The observations (a) - (f), above, strongly indicate that the dispersion of water through the "dense layer" membrane and the strength of polymer-water interactions at lower hydrations inhibit the formation of hexagonal ice even when the hydrated polymer is cooled to -50°C . Such behavior is reminiscent of that observed and previously studied (3,4) in concentrated ionic solutions which, upon supercooling, lead to the formation of viscous, supercooled liquids and, at lower temperatures, glasses having a "frozen-in" order similar to that of the solution structure. Indeed, the spectral similarities of the -10°C included water spectra to that at $+25^{\circ}\text{C}$ suggest that upon cooling neither hexagonal ice nor any strong, new water structures are formed. Rather, water molecules remain ordered within the membrane with bondings and local orderings similar to that at room temperature but with decreasing temperature, a gradual reduction in the average vibrational amplitudes occurs. Such a gradual reduction in average Debye or similar amplitudes would thus account for the sharpening of the three torsional components in going from $+25^{\circ}\text{C}$ to -10°C in a similar manner as observed previously, as the amount of water was reduced from 10 to 5 wt.% in the $\text{CA}_{2.5}$ membrane during which the population of the primary H_2O molecules coordinated with polymer OH groups was relatively favored. Initially, such torsional maxima, associated with primary polymer-water coordinations, sharpen and intensify with decreasing temperature while any secondary H_2O - H_2O coordinations and/or water-like clusters still give rise to a broad background upon which such maxima are superimposed. However, in passing from -10°C to -50°C , the 351 cm^{-1} component further sharpens and relative intensities of the higher two frequencies decrease in accord with a Boltzmann population effect as the temperature decreases. However, at -50°C a peak at 510 cm^{-1} (between the center of the torsional peak of ice and water), appears and may correspond to a low temperature coordination of the secondary waters or clusters. It should be recalled that in the interpretation given to the 25°C spectra it was noted that the three torsional components at 522, 415, and 351 appeared shifted down in frequency from those characteristic of pure water which occur respectively at 860 cm^{-1} , 590 , and 454 cm^{-1} . Where this reduction in frequency could reflect

polymer H_2O coordinations weaker than those in normal water, it was simultaneously noted that the residence time (average bonding period) for such water molecules was much larger than that characteristic of normal water. In part, this larger residence time was associated with a larger average jump length for water molecules in the membrane which would undergo activated jumps between successive polymeric OH group sites than in water. However, the above observations do not rule out the possibility that the water-OH bonding may be stronger than water-water bonding in pure water, such that water molecules may be bonded through their oxygens to polymer hydroxyl groups more strongly than similar coordinations in pure water. However, if the water protons were free to execute large vibrations as a result of a lower degree of coordination or on a time average being less bonded than 4-coordinated species characteristic of pure water, then the frequencies corresponding to the torsional oscillations of their protons about the center of mass could occur at a lower frequency than those observed in normal water (as shown in Figure 4). Thus, while such librational frequencies would appear lower, the stronger coordination of such water molecules through their oxygens to the primary polymer hydroxyl groups could give rise to a larger residence time as a higher activation energy would be needed in order to break such polymer-water bond prior to an activated jump.

The above observations on the temperature dependences of the included water are in accord with N.M.R. measurements made by Peterlin and Yasuda (19). These authors have noted a broader N.M.R. signal for water in polymers typical of those used for desalination membranes. Indeed, not only was the signal of water in such polymers broadened relative to normal water, but certain polymers showed a doublet which the above authors argued might occur due to the fact that certain of the water molecules or certain motions of such water molecules had preferred orientation. Further, these authors note that the N.M.R. signal of such water in cellulose acetate did not show any abrupt or appreciable changes down from $-90^\circ C$ where an abrupt broadening then occurred. This, they interpreted as indicating that water exists in such a manner in such membranes that freezing does not occur and the molecular motion of the absorbed water is not abruptly influenced until the temperature dropped far below $0^\circ C$.

In summary, the above neutron scattering results strongly emphasize that at lower hydrations the water in "dense layer" desalination membranes must be, in terms of coordination and diffusive kinetics, considered significantly different from normal water. The majority of H_2O molecules are coordinated directly to polymeric OH groups and their diffusion takes place uniformly throughout the membrane matrix by activated jumps between such hydrophilic sites. The bonding and coordination of H_2O molecules to polymeric hydroxyl groups appear more unique in its local ordering than the bonding characteristic of pure water which may imply that this bonding is primarily determined by the local polymeric segmental structure and is only secondarily, at best, influenced by longer-range ordering, as previously noted. It is clear that the H_2O molecules migrate throughout the polymeric matrix in a manner functionally described in terms of a jump diffusion model. Values of the self-diffusion coefficient

associated with such motions are much lower than those associated with normal water. This, in turn, reflects a combination of factors including a longer residence time, a smaller degree of free volume, and an increased jump length relative to normal water. In addition, at lower membrane hydrations where swelling is not pronounced, the free volume may be also sufficiently limited to inhibit formation of clusters and/or secondary water coordinations to an extent that they could readily form ice crystallites upon freezing.

4) The Dependences of the Bonding and Diffusive Kinetics on the Degree of Acetylation of "Dense Layer" Cellulose-Acetate Membranes and on the Concentration of Included Water

In order to determine the effects of varying degrees of acetylation on the bonding and diffusive kinetics of water in "dense layer" CA membranes, N.I.S. measurements were made and compared for the following three samples:

- 1) CA_{2.68} "dense layer" material (cast from A-432-130B) and containing 8 wt.% water (e.g., 3.8 H₂O's per OH group).
- 2) CA_{2.5} "dense layer" material (cast from E-398-10) containing 10 wt.% water (e.g., 2.9 H₂O's per OH group).
- 3) CA_{1.7} "dense layer" material (cast from E-320) containing 24 wt.% water (e.g., 2.5 H₂O's per OH).

The inelastic spectra are shown in Figure 5 and the corresponding curves of Γ vs. K^2 are shown in Figure 6. The following trends and features should be noted and compared with the results for the CA_{2.68} material discussed above and shown in Figures 1 and 2.

(a) In going from the CA_{2.68} to the CA_{2.5} to the CA_{1.7}, the density of OH groups increases and the equilibrium water content also increases. Hence, the degree of swelling of the membrane due to the included water also increases and an increase in free volume occurs. However, it should be simultaneously noted that with increased deacetylation or OH group density, the crystallinity of "dense layer" materials strongly decreases and, hence, the amount of free volume (available for water adsorption) associated with amorphous regions would increase. Unfortunately, precise quantitative estimates of such increases in free volume that occurs on going from the CA_{2.68} to CA_{1.7} are difficult to determine and are not available. However, in the limit of zero OH group content, H₂O molecules in amorphous regions would not involve direct OH-H₂O coordination and would be primarily combined by free volume and by weaker polymer water interactions. In contrast, at higher OH content (e.g., the CA_{1.7} material) the free volume in the immediate vicinity of an OH group in the amorphous region may be sufficiently larger to permit primary-secondary water coordinations and/or clusters to form.

(b) As shown in Figures 1 and 2 and discussed above, for 5% water in a CA_{2.5} "dense layer" membrane in the vicinity of 400 cm⁻¹ (e.g., channel 53), there appears to be a superposition of a larger number of sharper and better resolved torsional components than observed for normal water. The narrow widths and better resolutions of these maxima suggested that such coordinations were more unique with regard to distortion and variation of O--O distances than are the corresponding, more coordinated species characteristic of normal water. As the concentration of water was increased to 10 wt.% (Figure 2), while the above maxima persist, they became broader and more poorly defined. This concentration behavior was again in keeping with the presence of more than one type of coordination for water in the membrane material. Thus, at 5 wt.% loadings, where there are approximately 1.5 waters per OH group on the average, the majority of waters would be coordinated directly to OH groups. However, as the concentration is increased to 10 wt.% (e.g., three waters per OH group) the probability of forming secondary H₂O-H₂O coordinations and/or clusters would be enhanced. Such clusters, it was postulated, in analogy to normal water could involve a broader distribution of O--O distances and bond strains and, hence, would give rise to broader spectral components.

(c) Relative to the CA_{2.5} material with 10% water as the OH content is slightly reduced in going to the CA_{2.68} material, only slight, if any, variations are observed in the inelastic frequencies. Thus, again the H₂O appear primarily bonded to polymer OH groups and a degree of secondary water coordinations and/or clusters occur as well. However, the curve of Γ vs. K^2 appears shifted below that for 10 wt.% water in the CA_{2.5} material in keeping with a decrease in the self-diffusion coefficient, D , for the included water and an increase in the residence time, τ_0 . In accord with the argument of Yasuda et al (13,14), as discussed above, the decrease in D could in part reflect a decrease in the membrane free volume available for the diffusion of H₂O's. Simultaneously, the increase in τ_0 would reflect an increase in the activation energy for delayed diffusion associated with a slight increase in the separation and in the potential barrier between the potentials corresponding to the bonding sites between which the activated jumps occur.

(d) The spectra for 24% water included in a CA_{1.7} membrane corresponds to a case where larger numbers of secondary coordinations and/or clusters could be expected. According to the arguments of Yasuda et al (14), at this higher hydration, one would be closely approaching the "boundary line" between "lower hydration regions" (where the transport would involve the diffusion of water molecules along the polymer structure) and "higher hydration regions" (where bulk flow through a swollen membrane could contribute to the transport process). Indeed, at this concentration the multiplicity of sharper maxima, characteristic of the inelastic spectra for the lower loadings of water (e.g., 5 wt.% in the CA_{2.5} cellulose-acetate membrane), is lost and replaced by a broad librational maximum peaked in the vicinity of 400 cm⁻¹ or channel 53. Further, a comparison of this broad torsional maximum to the corresponding spectral region for water shows that the three torsional components at approximately 870, 605 and 460 cm⁻¹ with four coordinated

species in pure water are not observed. Indeed, the broadness of the inelastic frequencies for the included water in the CA_{1.7} membrane in the spectrum compared to normal water is similar to the situation observed when normal water is heated to higher temperatures and the four coordinated species become progressively disrupted and broken down.

(e) In Figure 6, the curves of Γ vs. K^2 are compared for 10% water in the CA_{2.5} membrane for 24% water in the CA_{1.7} membrane and for pure water. It is observed that with increasing water content (in going from the CA_{2.5} to the CA_{1.7} membranes) the corresponding curve of Γ vs. K^2 lies increasingly higher. This in turn corresponds to an increase in the self-diffusion coefficient, D , and a strong decrease in the residence time, τ_0 . Such behavior is in keeping both with the trends in the inelastic spectra, discussed above, and with the previous tentative model to describe the transport of water in the CA_{2.5} membranes.

The above results emphasize the twofold influence of the membrane under conditions of medium hydration where it has not been strongly swollen. To a first approximation, the extent and size of its amorphous regions must determine the average size of such secondary coordination groups or clusters and the average number of H₂O molecules in them. However, the interactions of such clusters with OH groups and the internal surfaces of such amorphous regions give rise to a distortion and/or disruption of the local ordering of such clusters relative to that which would be characteristic in normal water.

Thus, at the hydration corresponding to the 24 wt.% water in the CA_{1.7} membrane, the majority of H₂O's present are in secondary coordinations or clusters. Hence, the sharp maxima characteristic of lower coordinations where most of the waters were directly connected to OH groups, while present, would be obscured by the spectral contribution of such clusters, which in addition would have local coordinations which would be less ordered and effectively broken down relative to those found in normal water at lower temperatures due to interactions with neighboring hydroxyl groups of the membranes. In essence, a "breaking effect" or disordering of the local H₂O-H₂O coordinations characteristic of pure water would have resulted as a result of a competition or a mismatch between the structure of water and interactions of the amorphous morphology of the membrane.

It should be recalled that relative to the CA_{2.5} membrane at 10 wt.% water concentration, the CA_{1.7} membrane has about 24% water concentration. At the higher hydration in the CA_{1.7} "dense layer" material, there is a good probability that water clusters should exist. Such water clusters, due to their interaction with the surrounding polymeric material, however, would have local orderings broken down relative to pure water. Despite such weakened coordinations, the free volume constraints on the self-diffusion coefficient would still strongly suppress their self-diffusion coefficients relative to normal water as the constraints of the surrounding polymer would limit the number of vacant spaces into which a water molecule, once it has broken a bond or bonds from the cluster, could jump to. However, in view of the proximity of water-water coordinations, the average distance between adjacent bonding sites for a water molecule migrating through the membrane could be

strongly reduced; in addition, the average distance between polymeric OH-OH groups in the membrane material of higher hydration is decreased. Thus, a large decrease in the residence time would occur as a result of a decrease in the average activation energy. These factors would then contribute to a strong increase in the diffusive mobility of the transport of water molecules through the membrane material even though, in the case of the present CA_{1.7} material, appreciable swelling to the extent that bulk water flow could exist would be excluded.

5) Differential Scanning Calorimetric Measurements (D.S.C. of the Transitions Characteristic of the "Dense Layer" Materials)

Both D.S.C. and neutron scattering measurements were made in order to characterize the "dense layer" material used in the present investigations. It is clear from the above discussion that alterations of polymer morphology, of free volume, or of the degree of acetylation can strongly influence both the bonding and the diffusive transport of H₂O molecules in such materials. Further, it is also known that a particular casting process and the solvent used may strongly influence both the degree of crystallinity in such materials and the free volume connected with amorphous regions and, hence, strongly influence the water transport in such materials.

In this regard, Sauer and Morrow(23) have made extensive studies of the structure and morphology of membranes and their variations related to different methods of manufacture using cellulose and cellulose triacetate and using differential scanning calorimetry, x-ray diffraction, and dynamical-mechanical techniques. Typically, they find that for cellulose acetate the melting endotherm occurs near 230° C, while a glass transition occurs near 190° C. The melting endotherm near 230° C could be intensified by annealing at temperatures in the range 150-200° C.

A melting endotherm was also observed in samples that were annealed in water at temperatures of 70-100° C; and, hence, even under these conditions the material contains ordered regions or crystallites which are too small in size to be detectable by x-rays. The presence of water in the membrane tends to have a plasticizing effect and decreases the glass transition temperature, thereby increasing free volume.

In the present investigation, the D.S.C. measurements were made on the "dense layer" CA materials using a DuPont 900 Thermal Analyzer. The results of the D.S.C. measurements on "as cast" unheat-treated CA_{2.08} and CA_{2.5} "dense layer" materials shown in Figures 7-8. Upon heating (Figures 8 and 9), a broad second-order glassy transition is observed at about 40° C for the CA_{2.5} material. Further, when the membrane has been exposed to either a humid atmosphere or to water, this transition is nearly obscured by a broad endotherm with a minimum at about 60 to 80° corresponding to the desorption of H₂O. In addition, at higher temperatures, an additional second-order transition is observed in the vicinity of 180°, followed by a first-order transition at 220°.

As shown by the second curve in Figure 8, if the sample is heated through the melting transition at 220° , allowed to cool and then reheated, the glass transition, near 40°C , is lost, and the higher temperature transitions appear intensified.

As shown by the third curve, the sample can be heated up through the 40° transition, and so long as the higher transition temperatures are not exceeded, the 40° transition is not lost. Further, a wet sample can be heated through 40° transition and, provided the higher 180° temperature is not exceeded, it can be reversibly hydrated and dehydrated.

The neutron scattering results complement the above D.S.C. measurements. Previous measurements on more crystalline cellulosic materials show well defined inelastic frequencies corresponding to intramolecular and skeletal chain vibrations characteristic of well ordered chains packed in crystallites. In contrast, the neutron spectra of the cellulose-acetate "dense layer" materials are characterized by the near-absence of any such well defined vibrational frequencies and a broad distribution, peaking nearly at kT (e.g., channel 70) which approaches a shape characteristic of nearly free segmental motion. Thus, the large amorphous regions associated with the 180°C at the 40° transitions are also associated with free segmental motions and rotations than in more crystalline materials.

Corresponding D.S.C. curves for an "as cast" (from E-320) $\text{CA}_{1.7}$ "dense layer" material are shown in Figure 9. A degree of similarity existed in both the number and types of transitions observed for the two samples. In the vicinity of $217^{\circ} - 240^{\circ}\text{C}$, a first-order transition is observed characteristic of the melting of crystallites. Below this transition in temperature, a broad second-order transition is observed typically in the region between 170° and 200°C . In general, existence of these two types of transitions appears common to cast prepared cellulose-acetate "dense layer" materials. However, both their characteristic temperatures and intensities may vary, depending both upon the material, the degree of acetylation, and the casting procedure.

In addition to the above transitions, a third (second order) transition is observed at lower temperatures and appears to strongly correlate with and depend upon the casting procedures. Thus, for the $\text{CA}_{2.5}$ membrane cast from the Eastman-398-10 in an acetone solution, this transition occurs in the vicinity of $40^{\circ} - 60^{\circ}\text{C}$. A similar transition was observed for the membrane cast from Eastman-320 in D.M.S.O. solutions in the vicinity of $145^{\circ} - 135^{\circ}\text{C}$. It is to be emphasized (as shown schematically in Figure 8) that if care is not taken to make the D.S.C. measurements under vacuum conditions, the loss of adsorbed water upon heating the membrane materials during a D.S.C. run can readily obscure such transitions. An important observed characteristic of these lower temperature second-order transitions is that they are preserved provided the sample is not heated above the temperature corresponding to the melting of the crystallites. However, if the cast membrane is heated above the crystalline melting point and then cooled, the lower

temperature second-order transitions are lost and only the transitions characteristic of the higher temperature second-order and melting of crystallites are then preserved.

The above results emphasize that in such cast "dense layer" materials there are effectively "two types" of amorphous regions: those regions corresponding to larger free volumes and associated with lower second-order glass transitions and regions associated with a smaller free volume and, hence, with the second-order glass transition in the vicinity of 180°C . The larger free volume regions associated with the lower temperature transition appear to be formed during and peculiar to the casting process. Both of these regions must play a role in determining the free volume available for the diffusion of H_2O molecules and/or ions. However, more precise D.S.C. measurements are required to determine quantitatively the relative magnitudes of these transitions to allow the relative percentage of the membrane material associated with each type of amorphous region to be estimated. However, the preliminary results to date tentatively suggest that the majority of polymer segments in the membrane may be associated with the higher second-order transition and hence crystallites and the larger amorphous regions constitute the more minor components.

Curve II of Figure 9, shows a D.S.C. curve of the original "as cast" membrane (whose D.S.C. trace is given in Curve I) after it has been soaked in water. The following changes in the transitions shown in Curve I should be noted. The melting of the crystallites now occurs at a higher temperature (e.g., 240°C vs. 218°C). The lower of the two second-order transitions has become broader, less intense, and slightly shifted to lower temperature. In contrast, the higher second-order transition which originally occurred at 170°C now appears to be much sharper and shifted up in temperature by 30° to approximately 200° . Thus, the most pronounced effect of the included water has been to decrease both the average size and dispersion of free volume associated with the higher of the two second-order glass transitions and to slightly enhance the crystallinity of the sample. This appears to have happened in part at the expense of larger free-volume regions that were originally associated with the lower second-order transition.

The larger magnitude (Curve II, Figure 9) of the second-order transition at 200° in the annealed sample strongly suggests that the amorphous regions associated with it could well constitute the dominant morphological feature of the membrane and, hence, be the prime feature controlling and influencing the diffusive mobility of H_2O molecules and/or ions in the material. Further, a preliminary comparison of the D.S.C. curves in Figure 9 for the membrane cast from E-320 with corresponding curves reported in Figure 7 for the membrane cast from E-398-10 suggests that the increased degree of acetylation of the latter "dense layer" material relative to the former has resulted in a higher degree of crystallinity(43) and a corresponding lower amount of amorphous regions that would be associated with the 180° second-order glass transition. Then, indeed, if the diffusion process is associated

with such amorphous regions (43) and their stabilization is associated with the crystallites present, the higher salt rejection rate of the latter "dense layer" material as well as its ability to swelling can be accounted for in part.

In essence, the "as cast, dense layer" materials may be viewed to a first approximation as being composed of the following three regions.

1) The larger amorphous regions associated with the higher of the two glass transitions and with smaller free volume. These regions may be the most influential in determining the salt rejection and flux characteristics of the "dense layer" material. Thus, the free volume associated with such regions may be sufficiently large to sterically allow the activated diffusion of H_2O 's along the hydrophilic groups in these regions, but may be sufficiently small to restrict and confine the diffusion of hydrated ions in the "dense layer" materials to the more open areas of this region and, hence, to a more tortuous diffusion path.

2) The smaller amorphous regions associated with the low temperature glass transitions and larger free volume. These regions appear to be strongly dependent upon the casting procedures, the type of solvent used, and upon heat treatment. Thus, if the materials are heated to near their crystalline melting points, these regions appear to "collapse", reduce in free volume, and contribute to the T_g near $190^\circ C$. They are also reduced in a similar manner but more gradually by a heat-treatment in water at lower temperatures. The relative amount of such "larger free volume amorphous regions" can depend strongly on the rate at which the casting solvent is removed and on subsequent heat treatment in water. Thus, if the solvent is rapidly removed at low temperature by washing in water, the contributions of such larger free volume regions could be considerable. In contrast, if the solvent is gradually evaporated such regions would in turn gradually collapse and reduce in free volume. In like manner, heat treatment at temperatures at or below $90^\circ C$ in water would reduce the free volumes of such regions but not allow sufficient rapid growth of crystalline regions so that the net amorphous fractions through which permeates diffuse, is reduced. Indeed, it is the reduction of free volume associated with such regions that may largely account for the increase in salt rejection and a decrease in flux upon heat treatment. Thus, in such regions, the larger, free volume may permit the rapid diffusion of ions and a nearly "bulk flow" of water. However, when this free volume is reduced by heat treatment, steric constraints now reduce the salt permittivity and confine the diffusion of H_2O 's to the activated diffusion process described above.

3) The small crystallites that give rise to the first order transition at $220^\circ C$ may serve to stabilize the free volume regions described in (1) and (2) above such that when they are melted the amorphous regions associated with the lower T_g and, to a lesser extent, the amorphous regions associated with the higher T_g irreversibly reduce in free volume.

For optimum membrane performance, the membranes are heat treated in water (which acts as a plasticizing agent) at temperatures sufficiently high to reduce free volume as described above, but yet sufficiently low so that a larger increase in crystallinity and reduction in amorphous regions does not result.

6. The Influence of NaCl on the Bonding and Diffusive Kinetics of the Included Water in a CA_{2.5} Membrane

As shown in Figure 10, it is seen that very little difference in inelastic frequencies results for the spectrum of 10% included water in the cellulose CA_{2.5} "dense layer" material and the same "dense layer" material containing 10 wt.% NaCl solution of 1.5 m equivalent NaCl concentration. In view of this similarity in frequencies it should be recalled that in previous studies of ionic solutions (as a function of concentration) significant departures in the inelastic frequencies from those characteristic of pure water typically occur at concentrations above 1.0 m for sodium chloride and a number of other ionic salts. In addition, for the 10% sodium chloride solution in the CA_{2.5} membrane it should be noted that per NaCl there are approximately 30 H₂O's and 10 OH groups belonging to the polymer. Thus, most of the H₂O's present may be distributed away from the sodium and coordinated to polymeric OH groups as for the CA_{2.5} membrane containing only pure water. The degree of hydration of the sodium may be limited both by steric considerations determined by local free volume in the polymer and the ability of such free volume to support a fully hydrated cation as well as the distortion and resultant breaking down of sodium-water hydration layers due to possible interactions between hydrated sodium and the hydrophilic groups of the polymer.

Thus, the similarity of the inelastic frequencies emphasizes that while emission spectroscopy had shown the presence of the NaCl in the polymer, nevertheless only a small fraction of the H₂O's are bonded to a sodium at any instant. Indeed, the majority of water molecules are coordinated to polymer hydroxyl groups in a fashion similar to that observed in the absence of sodium.

In contrast to the similarity observed in inelastic frequencies, a significant variation is seen as a result of the included sodium relative to CA_{2.5} membrane material containing 10% pure water in the diffusive kinetics. As previously noted and as shown in Figure 3, the curve of Γ vs. K^2 for 10% water in a CA_{2.5} membrane lies well below the corresponding curves for pure water. In terms of a jump diffusion mechanism this behavior in part reflects a strong decrease in the self-diffusion coefficient and a large increase in the residence time. As discussed previously, in accord with the arguments of Yasuda et al (13,14,19) the strong decrease in the self-diffusion coefficient relative to pure water would result from the influence of free volume on the self-diffusion coefficient. Thus, in contrast to pure water, the steric constraints in a polymer membrane may limit diffusion by limiting the free volume into which a water molecule can jump once it has broken from a group to which it has been coordinated. The larger value of τ_0 reflects a larger distance between consecutive bonding sites between which a water molecule could jump in a polymeric

membrane than would be present in pure water. Thus, in accordance with the arguments of Samoilov(42), when considering activated jumps between two potential minima separated by a barrier, both the depth of a potential as well as their spacings are important in determining the effective activation energy. If two wells were infinitely separated, the removal of a water molecule from such a well would require a larger energy than that required to penetrate the much lower barrier between potentials which are more closely spaced.

The addition of NaCl to the 10% water contained in the CA_{2.5} membrane appears to increase the D and decrease the τ_0 relative to the case of pure water alone in a real and significant manner. In essence, this could be termed a "structure-breaking" behavior or an increase in the diffusive mobility of the included water as a result of the addition of the sodium chloride. Indeed, this trend is just in the opposite direction to that observed upon the addition of sodium chloride to pure water in ionic solutions where it produces a "structure-making" effect, resulting in a decreased D and an increased τ_0 . This result at first seems surprising(44). However, it is readily accounted for in terms of the above model for the jump diffusion of H₂O molecules in this cellulose-acetate membrane. The included ions, although not strongly hydrated at any instant, could provide symmetrical sites intermediate to adjacent polymeric OH groups to which an H₂O could jump, stay in residence for only a short time, and then quickly detach and pass on to the next site. Thus, in essence, such ion would provide intermediate bonding sites or potentials between the more widely spaced potentials corresponding to successive hydroxyl groups. In turn, this would effectively decrease the barrier between adjacent hydroxyl groups and decrease the activation energy(42,43). While this explanation must as yet be considered as tentative, it suggests that the presence of a salt in a membrane may change the diffusion of water molecules (in the absence of an osmotic pressure or applied pressure gradient) by effectively reducing the distance between bonding sites relative to the polymeric material alone. Further measurements are needed to confirm this tentative interpretation and to further study this interesting effect.

It has been reported that under an applied gradient the water flux in general decreases with increasing concentration of NaCl as the result of the increased concentration gradient and osmotic pressure. In contrast, however, careful tracer measurements(44) made under equilibrium conditions (equivalent to the conditions of the present measurements) indicate an increase in the water permeation with increasing NaCl concentration in accord with the present results.

7.) The Dependence of the Bonding and Diffusive Kinetics on the Molecular Weight of "Dense Layer" Cellulose-Acetate Membranes

In Figure 12, the spectra of neutrons inelastically scattered from the 10 wt% water in CA_{2.5} membranes cast from E-398-10 and from E-398-3 cellulose acetate are compared. The Eastman-398-10 has an average MW equal to 44,800. The Eastman-398-3 has an MW equal to 35,100. In Figure 13, the curves of Γ , the Lorentzian half-width at half-maximum of the diffusively broadened incident energy distribution, are shown as a function of the momentum transfer (K^2) for the included water in the two "dense layer" materials of different molecular weight. To complement the above neutron scattering measurements, D.S.C. warm-up curves are shown for the two "dense layer" membrane materials in Figure 4. In considering the data of Figures 12 to 14, the following features should be noted.

- (a) The intermolecular frequencies characteristic of primary polymer hydroxyl-H₂O coordinations at 522, 415, and 315 cm⁻¹ appear broader and less intense for the water in the lower molecular weight CA_{2.5} membrane than those previously observed for the water in a CA_{2.5} higher molecular weight membrane. Thus, it appears with decreasing molecular weight that the frequencies characteristic of the primary hydroxyl-water coordinations have deintensified relative to the broad component which was associated previously with secondary water-water coordinations and/or clusters. Such behavior suggests that in the lower molecular weight membrane, due to an increased free volume, a slightly larger percentage of H₂O molecules may be involved in secondary coordinations rather than primary polymer hydroxyl-water coordinations. A similar trend and broadening were observed previously with increasing membrane-water content as the number of hydrophilic sites was increased due to the formation of larger secondary water coordinations and clusters at higher membrane hydrations.
- (b) Figure 13 shows that the curve of Γ vs. K^2 for the water in the lower molecular weight membrane lies above that for the water in the higher molecular weight material so as to correspond to an increase in the self-diffusion coefficient. No significant change in the residence time associated with the jump diffusion of water molecules in these membranes is indicated. This behavior could well be associated with an increase in the average free volume which in turn would primarily contribute to an increase in the self-diffusion coefficient but would not significantly alter the average period or residence time that a water remained bonded.
- (c) The D.S.C. curves, shown in Figure 14, for these materials, indicate a broader and more enhanced second-order glass transition and smaller melting transition for the lower molecular weight material than those for the higher molecular weight material, in keeping with a slight increase of free volume for the former. As previously discussed, the membrane may be considered to a first approximation as having large areas of free volume formed during the casting procedure which is.

stabilized by the presence of small crystallites and through which water molecules can diffuse. Indeed, it is not surprising that the lower molecular weight is associated with a slight increase in free volume as it is known that in high polymeric materials an increase in the number of chain ends can give rise to an increase in the amorphous regions of the polymer and inhibit crystalline packing(46).

The above results which are in accord with the findings of F.S. Model et al(37) indicate that a reduction in molecular weight at a fixed degree of acetylation results in increased diffusional freedom of the water molecules and an increase in the average free volume associated with the amorphous regions of the membrane this both allows the relative number of secondary water coordinations to increase, and provides and increases the self-diffusion of such waters by the corresponding increase in free volume. Specifically, as the molecular weight decreases for a fixed degree of acetylation, the average free volume available for diffusion of water molecules also increases. This, in turn, as noted above, increases the diffusion of the water to the membrane matrix and, hence, increases the flux. However, secondary water coordinations and clusters are also favored. These, together with the increase in free volume, could also favor an increase in the salt flux through the membrane. Thus, it has been argued that hydrated salt ions are confined and diffuse through more open and larger free volume regions of the membrane which are water-rich. As a result, they travel a longer and more tortuous path than individual H₂O's. As discussed above, it has been argued that this difference in the diffusion mechanism for the ions and the water may, in large part, be the governing factor in determining the flux and salt rejection properties of such membranes. Thus, however, an increase in free volume due to either swelling or a change in molecular weight, as described above, may aid the diffusive mobility of the water, but such a change in free volume may also enable the salt ions to traverse a shorter path in the membrane and, hence, decrease the salt rejection properties. Additional measurements are needed to confirm this possibility.

8) Initial Investigations of the Effects of Heat Treatment on "Dense Layer" Cellulose-Acetate Desalination Membrane

It is known^(17,47-49) that the annealing or heat treatment of "as cast" asymmetric cellulose-acetate membranes constitutes one of the most important fabrication variables. In general, it has been determined that such annealing both reduces the water and salt fluxes but the latter more strongly so that the net rejection increases with annealing temperature. Further, it has been shown that both the temperature of the annealing and the time of annealing constitute significant variables. The annealing mechanism appears to be composed of two steps -- an initial steep change during which most of the changes in the water and the osmotic properties of the materials occur, followed by a slower change in which again the flux and salt permeations further decline. The higher the annealing temperature (typically in the range between 55 and 85°C) the more

rapid is the initial variation (17,47,48) Simultaneously, such annealing enhances the stress at yield for such membrane materials(48). Typically, such annealing of a porous membrane is done in a heated water bath (water being a nonsolvent capable of functioning to an extent as a plasticizer) and results in diminution of the free volume of the membrane material and, hence, in its permeability and permselectivity. It has been argued(47) that this occurs at a molecular level as the thermal energy causes translational motions of the polymer chains with the result that the polar groups on neighboring molecules approach each other and interact by dipole-dipole interactions. Such interactions decrease chain mobility and in a nonsolvent medium are irreversible because of the inability of the nonsolvent to solvate and intervene between the polar groups so interacted. Simultaneously, crystallites can increase in size and move closer together decreasing the mean diameter of the free volume through which permeation takes place. In general, during annealing water is gradually lost from the primary gel both because of the compaction described above and because the decrease in free volume sterically limits the size of clusters or aggregates that water can form in the membrane. A more discontinuous effect is the dramatic increase in salt retention which is observed when cellulose-acetate is heated above the lower glass transition (see Section III(5)).

Both the extent of the changes observed upon annealing and the temperatures at which they occur for a given polymer (such as cellulose-acetate) in turn depend strongly on the history of the casting process. Thus, for example, many current methods producing asymmetric membranes involve the gelling of a casting solution consisting of the polymer and a solvent (such as acetone or DMSO) on the substrate surface. As the acetone evaporates a concentration gradient of the solvent exists with the greatest concentration away from the air surface of the film and towards the substrate surface. Then, when such a film is removed it may still contain a large amount of acetone. If the film is then rapidly dipped in cool water (a nonsolvent) to rapidly exchange the remaining acetone and, hence, regions of large free volumes will be left corresponding to where the acetone was left in the polymer. Thus, the side formerly in contact with the substrate having the greatest concentration of the acetone will yield a porous surface. The side least rich in acetone will form the "dense" skin.

In contrast, the process used to form the "dense" skin materials in the present experiment allows the acetone to slowly evaporate either in air or in vacuum. In such a case, as the acetone is slowly and more completely leaving the gel, the polymers may compact and reduce their free volume gradually. Thus, a more "dense layer" material is formed and is also without the porous backing which may in fact have an average smaller free volume than the "dense skin" that would be formed on a porous asymmetric membrane. Indeed, when such gels from which the acetone had been removed by a slow evaporation process were subjected to heating for 4 minutes in water, at 80°C, very little change was seen in the equilibrium water content, in direct contrast to the behavior observed for "as cast" asymmetric cellulose triacetate films. This suggested that the slow removal of acetone indeed had allowed a reduction in free volume similar to that achieved by annealing for the asymmetric films. Prior to

studying the effects of annealing in detail, neutron scattering measurements were made to determine the extent to which the bonding and diffusive kinetics of water had altered before and after heat treatment in such materials made by the full evaporation from the gel of the acetone. The results indeed showed no significant change in the inelastic frequencies characteristic of primary water-OH coordinations or in the curve of Γ vs. K^2 and, hence, in the self-diffusion coefficients and residence times for the water that resulted from the annealing. Simultaneously, no significant change was observed before and after heat treatment on the D.S.C. curves for this material. These results emphasize that (a) it is important to realize that the effects produced by the annealing process in water flux and salt rejection while large and important are also strongly dependent on the nature of the prior casting process; and (b) the nature in which the solvent (e.g., acetone, etc.) is removed in turn can determine the free volume frozen into the resultant "dense skin" and the ability of the chains to relax and reduce this free volume. Thus, if the acetone is removed rapidly, as in commercial processes as by dipping in cold water to dissolve it out, regions of large free volume remain. These regions are undoubtedly associated with the lower glass transitions typically seen in the vicinity of 40 to 100°C, as discussed in Section III(5), which were observed to depend both in their magnitude and in their temperature, strongly on the solvents used to form the gel. In contrast, if the film is removed from the water and the acetone or solvent is allowed to gradually evaporate, the chain mobility is sufficient to reduce the free volume and produce an equivalent effect to that achieved by the annealing processes normally used.

Further experiments must be carried out to confirm these results and to study the magnitudes of the decreases in self-diffusion coefficients that would result when the solvent is first washed out and heat treatment is then used to reduce the free volume. Such variations, in accord with the theory of Yasuda et al(13,14), discussed above, should primarily affect the self-diffusion coefficient through the free volume factor and only secondarily, if at all, affect the residence times which are primarily dependent on the number, the separation, and the strength of bonding of the primary hydroxyl groups.

TABLE I

CHARACTERISTICS OF "DENSE LAYER" MATERIALS AND THE AMOUNT OF
THE INCLUDED WATER USED AS SAMPLES FOR N.I.S. INVESTIGATIONS

<u>Resins Used To Cast Membranes</u>	<u>% Acetyl Content</u>	<u>Average No. of Acetyl Groups/ Anhydroglucose Units</u>	<u>Average No. of OH/Repeat Molecular Segment (4 Anhydro- glucose Units)</u>	<u>Wt. % H₂O in Membranes</u>	<u>No. of H₂O Molecules per OH</u>	<u>No. of H₂O Molecules/Repeat Molecular Segment</u>
E-320	32.0	1.68	5.27	~ 24	2.3	12.1
E-398-10	39.8	2.5	2.0	~10	2.9	5.8
A-432-130B	43.2	2.68	1.3	8	3.8	4.9

FIGURE 1

The time-of-flight spectra for the neutrons inelastically scattered by the water included in the membranes is shown as a function of scattering angle at 25°C. The observed frequencies are indicated by the vertical lines. Spectra for water at 1°C, showing its inelastic frequencies, are shown for comparison.

INTENSITY IN ARBITRARY UNITS

10% H₂O in CA_{2.5}
RT

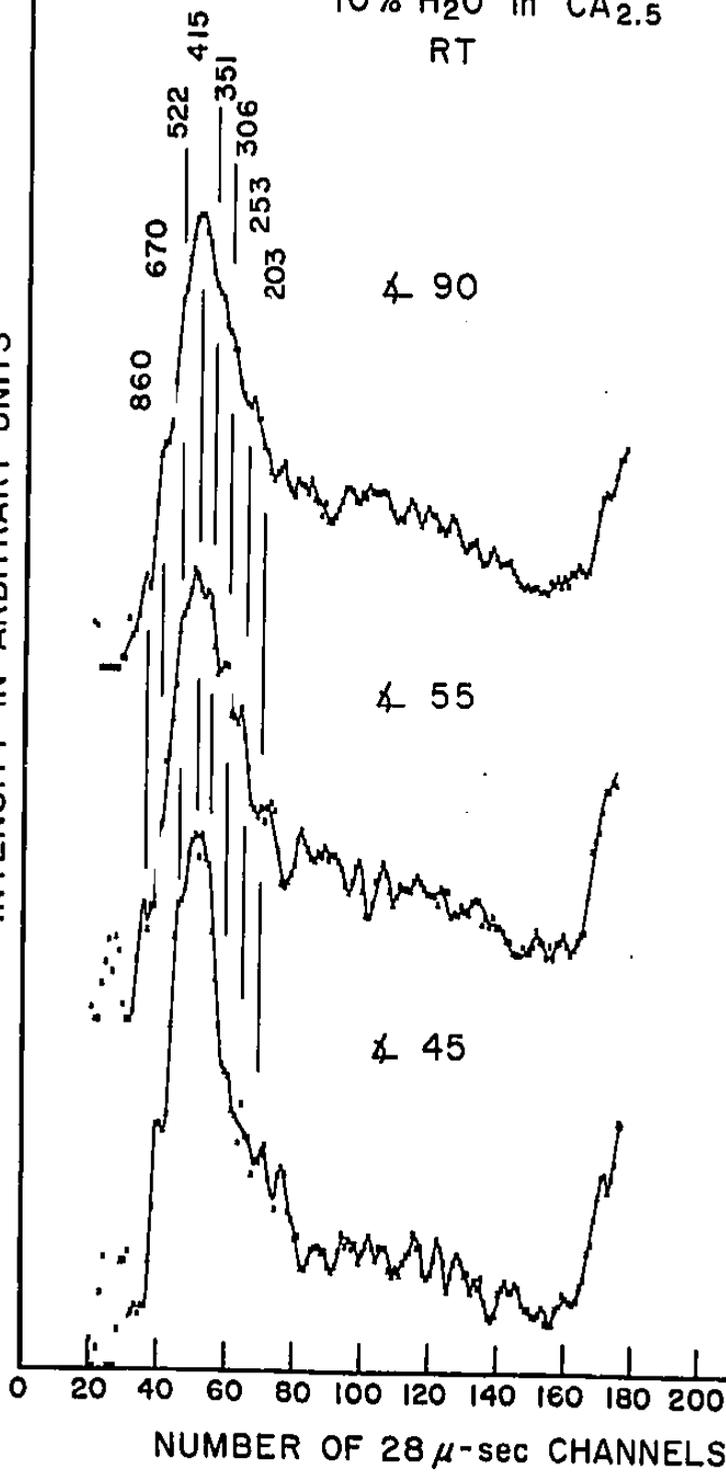


FIGURE 2

The time-of-flight spectra of neutrons scattered from included water in a cellulose-2.5 acetate membrane are shown as a function of concentration of the included water.

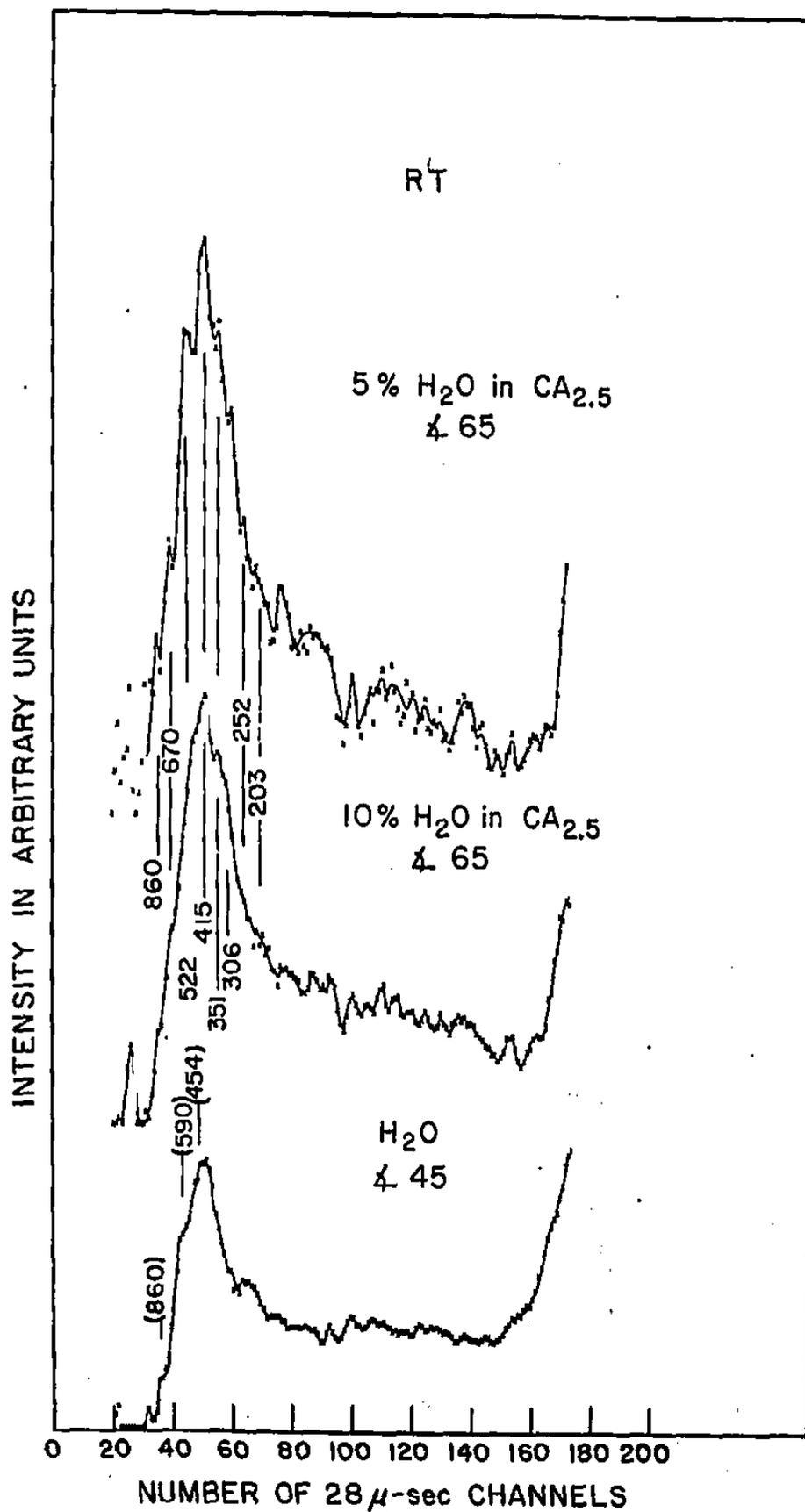
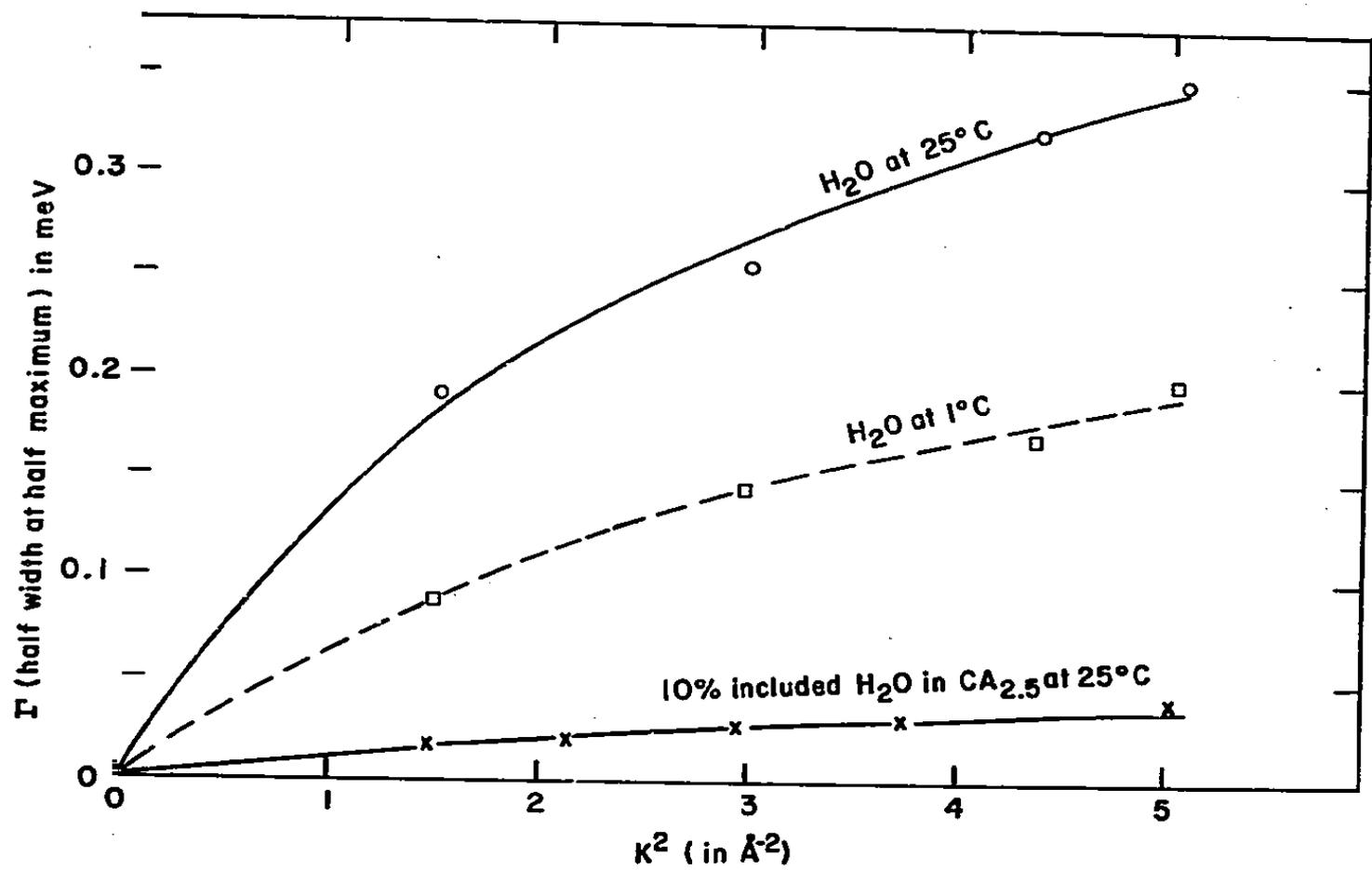


FIGURE 3

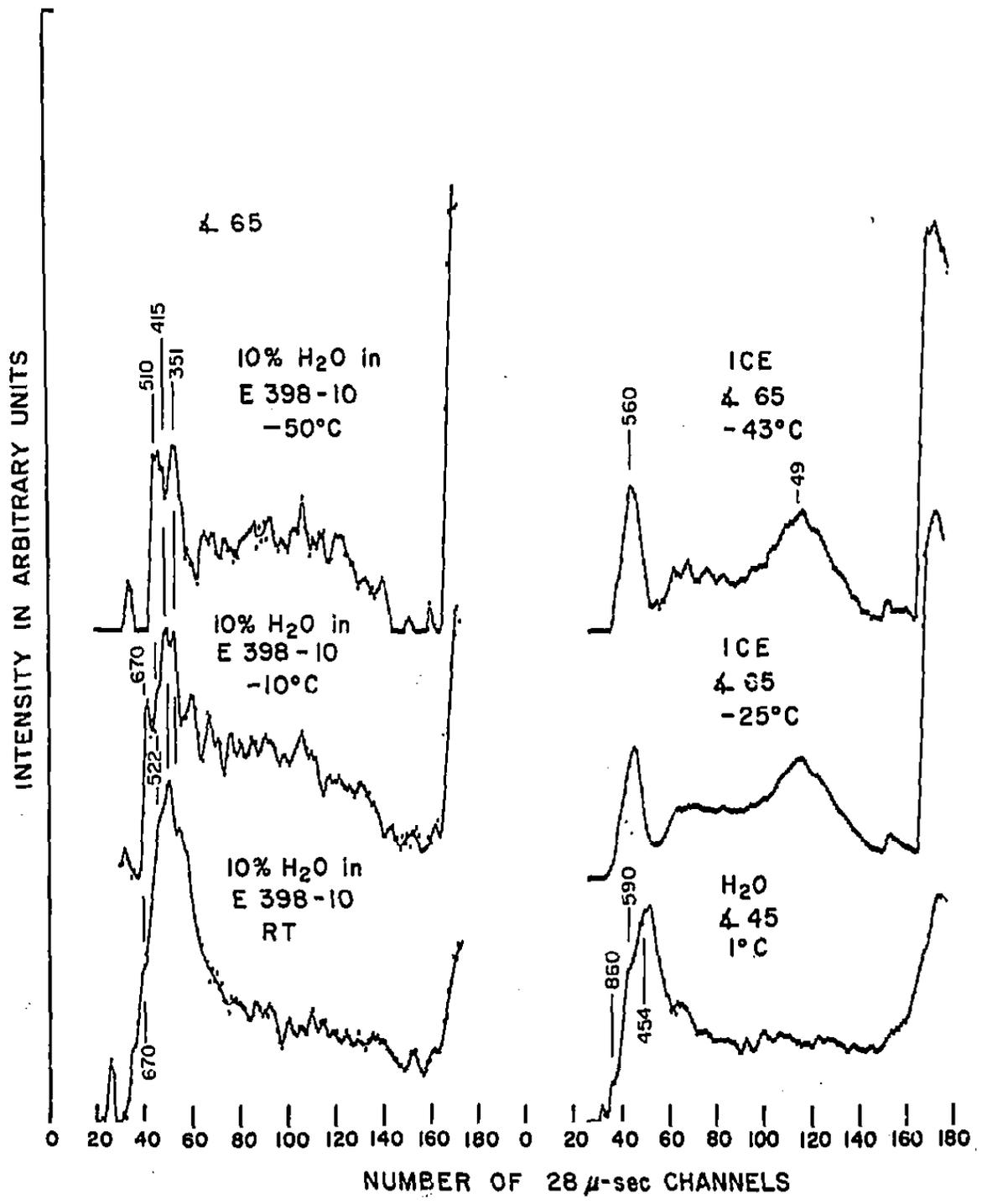
The dependence of the half-width at half-maximum, Γ , of the diffusively broadened incident energy distribution for neutrons scattered from the included water is shown as a function of K^2 and compared with the corresponding curves for water at 25°C and water at 1°C.



30-b

FIGURE 4

The time-of-flight spectra for neutrons scattered inelastically from 10 wt% water included in $CA_{2.5}$ membranes are compared at $+25^{\circ}C$, $-10^{\circ}C$, and $-50^{\circ}C$. In addition, spectra are shown for normal water and for hexagonal ice. It should be noted, as discussed in the text, that the spectra for the 10 wt% water at $-10^{\circ}C$ and $-50^{\circ}C$ are more similar to the spectrum for the 10 wt% water at $+25^{\circ}C$ than they are to the spectrum of either normal water or hexagonal ice (frequency in cm^{-1}).



40-b

FIGURE 5

The time-of-flight spectra for neutrons scattered inelastically from water; from 8 wt% in $CA_{2.68}$ membrane; from 5 wt% in a $CA_{2.5}$ membrane; from 10% water in a $CA_{2.5}$ membrane; and from 24 wt% water in a $CA_{1.7}$ membrane are compared. As discussed in the text, at low water concentrations, a multiplicity of sharper, well defined torsional components are observed in the vicinity of channel 50 corresponding to H_2O 's directly coordinated to OH groups. With increasing water concentrations, secondary water-water coordinations and/or clusters are formed having poorer local ordering than that characteristic of normal water. As a result, the sharper inelastic maxima characteristic of the low water concentrations are "lost" and replaced by a broad distribution.

INTENSITY IN ARBITRARY UNITS

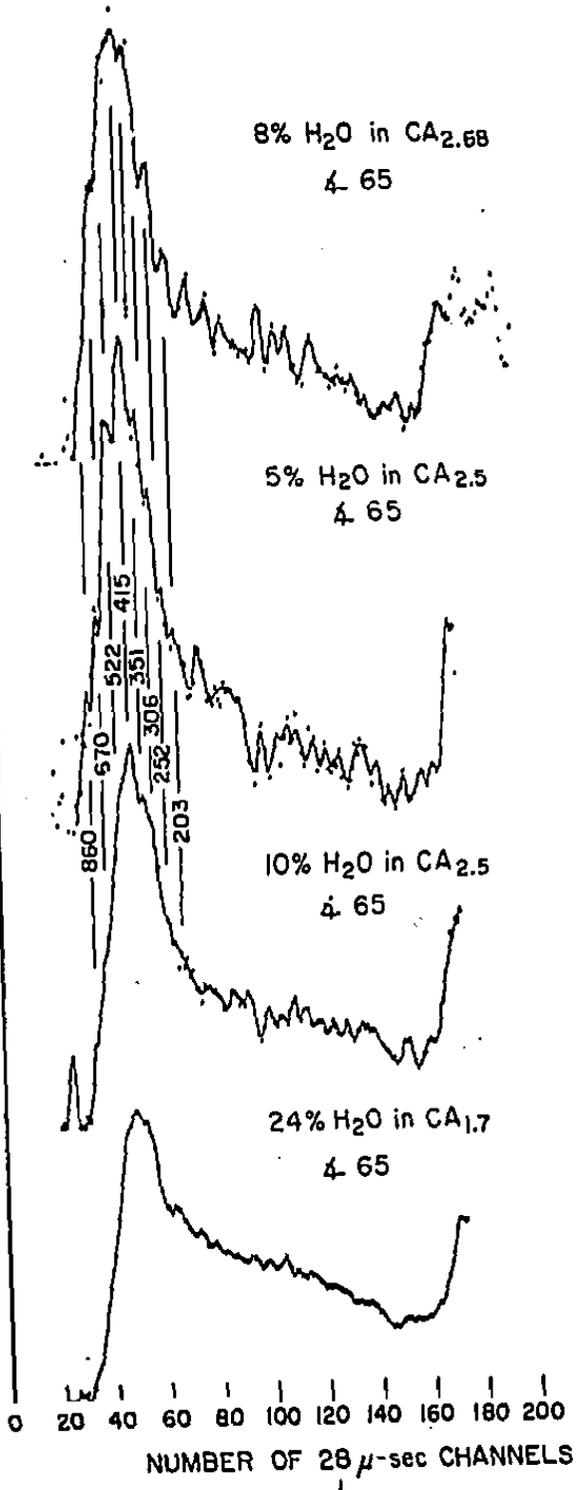


FIGURE 6

Curves of the Lorentzian half-width at half-maxima (Γ) of the diffusively broadened incident energy distributions as a function of the momentum transfer (k^2) are compared for:

- (a) 8% water in a $CA_{2.68}$ "dense layer" material
- (b) 10% water in a $CA_{2.5}$ "dense layer" material
- (c) 24% water in a $CA_{1.7}$ "dense layer" material
- (d) normal water at room temperature

The observed changes are discussed in the text.

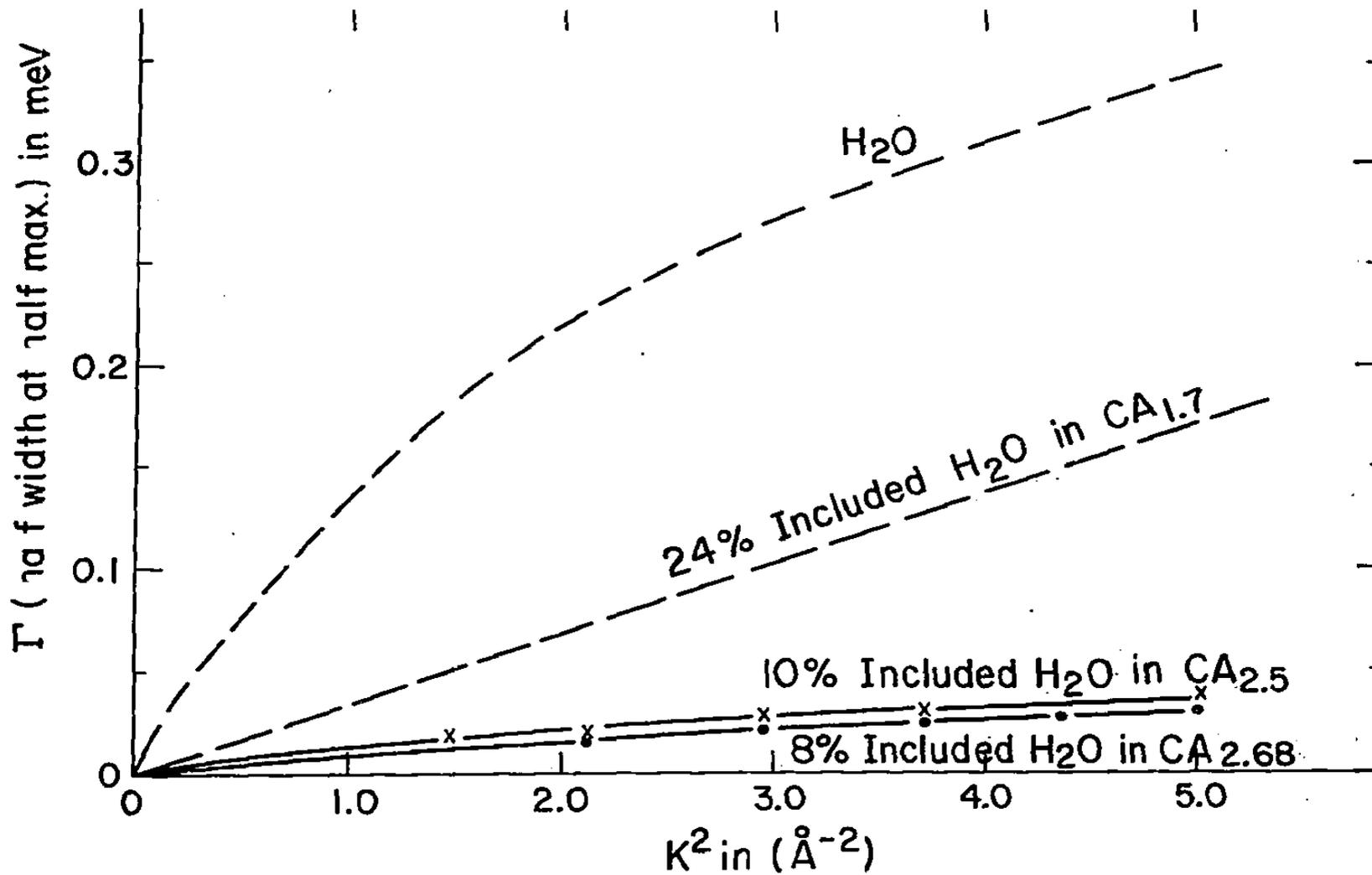
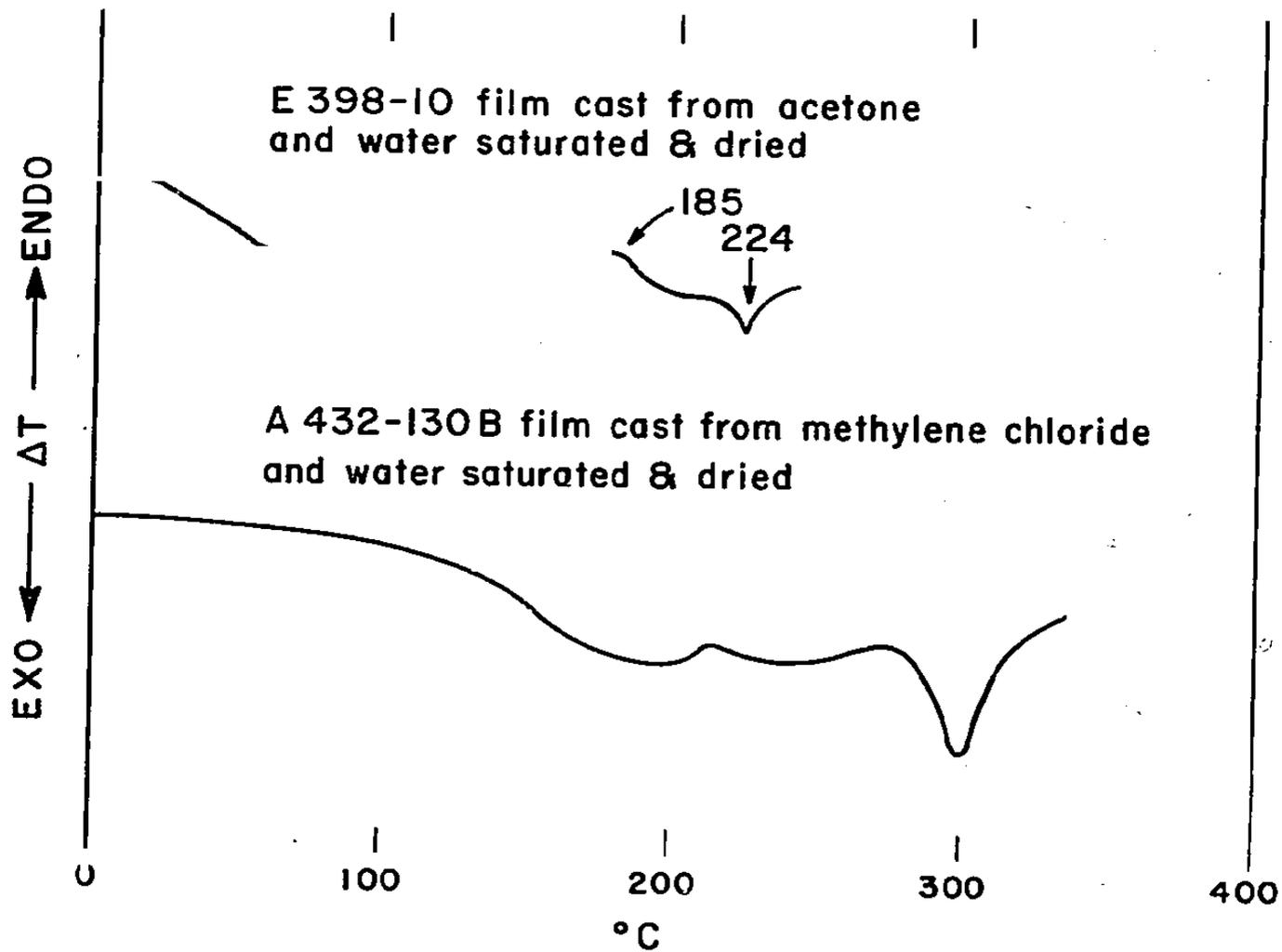


FIGURE 7

The differential scanning calorimetry traces are compared for "dense layer" materials cast from E-398-10 (CA_{2.5}) and A-432-130B (CA_{2.68}). A higher melting point and increase of crystallinity is observed for the CA_{2.68} relative to the CA_{2.5} material.



113-b

FIGURE 8

Differential scanning calorimetry traces for the "dense" membrane materials are shown schematically. The top curve shows the transitions observed upon heating the material through 220°C. The superimposed dashed curve in the vicinity of 60° to 80°C corresponds to the desorption of water when the membrane is wet, and the dashed curve in the vicinity of 180°C represents the loss of remnant acetone. The center curve corresponds to the D.S.C. trace obtained when the sample previously had been heated to 220°C, allowed to cool, and then reheated. It is observed that the transition in the vicinity of 40°C is lost. The third curve corresponds to a fresh sample that had been heated through the transition at 40°C but not through the transitions at 180 and 220°C. Under such conditions, the 40° transition is not lost.

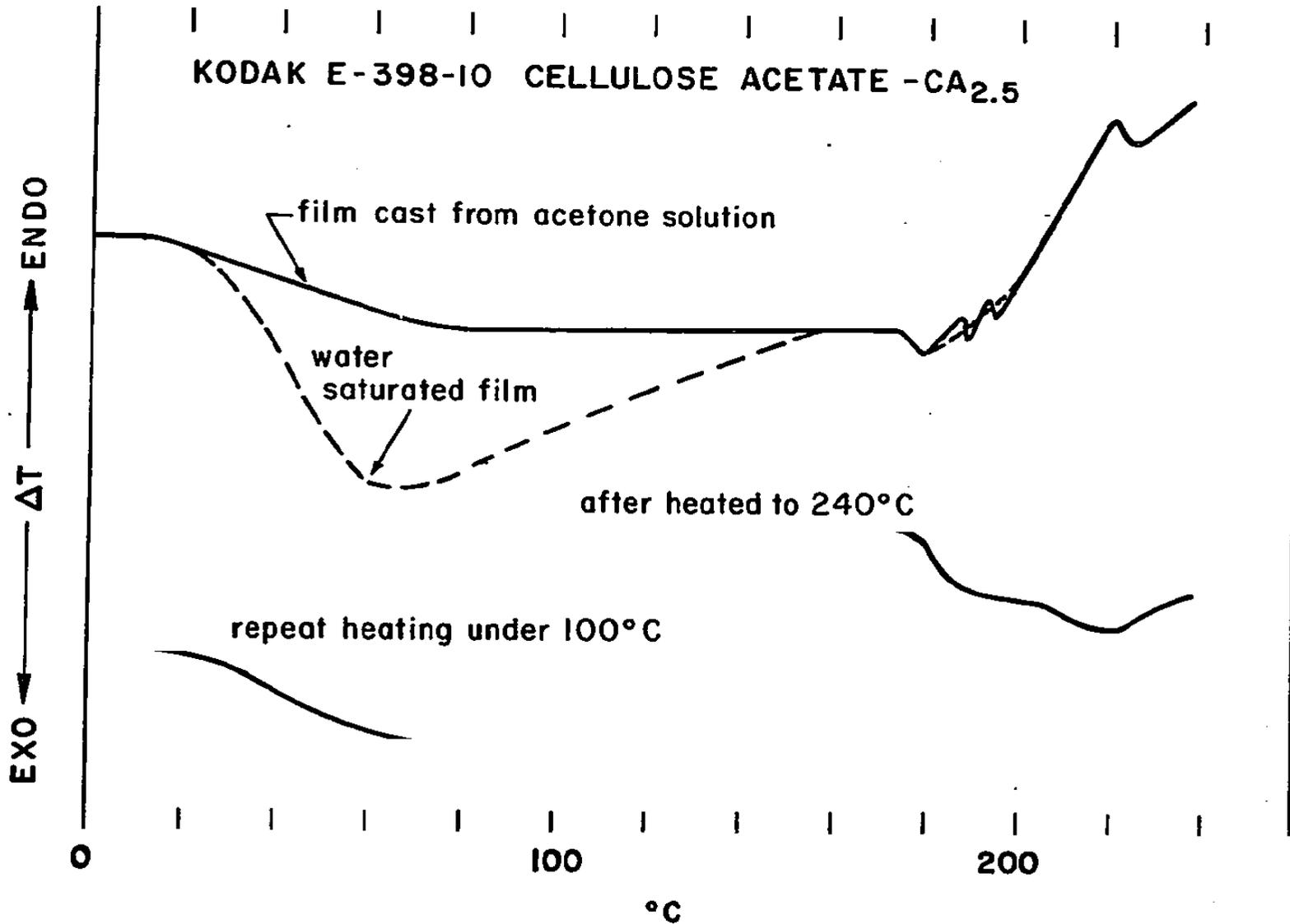
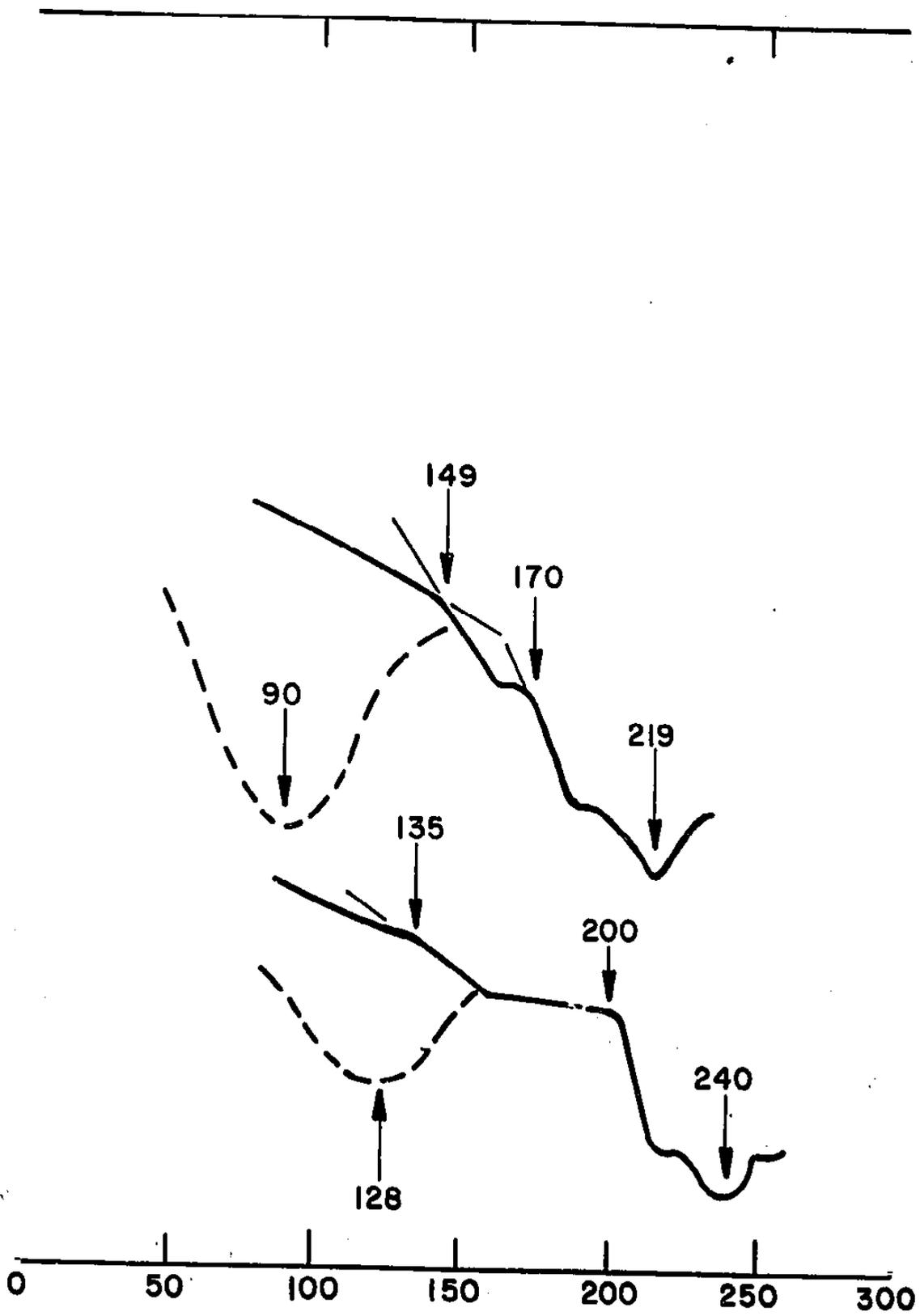


FIGURE 9

The differential scanning calorimetry traces are shown for a CA_{1.7} "dense layer" material cast from E-320 cellulose acetate. The top curve is for the "as cast" material from DMSO solution, and the lower curve is for the same material which further had been soaked for an extended period in water and then dried under vacuum at room temperature. Both solid curves represent measurements made under vacuum conditions in order to avoid water desorption (as shown schematically by the dotted line) which would obscure some of the lower temperature transitions in the D.S.C. traces. The individual transitions and their variations between the "as cast" and "soaked" sample are discussed in the text.

ENDO = ΔT = EXC



TEMPERATURE °C

45-B

FIGURE 10

The time-of-flight spectra for neutrons inelastically scattered from 10% water in a $CA_{2.5}$ membrane and from water molecules in a sodium chloride solution of 1.5 m equivalent concentration included in a $CA_{2.5}$ membrane are compared.

INTENSITY IN ARBITRARY UNITS

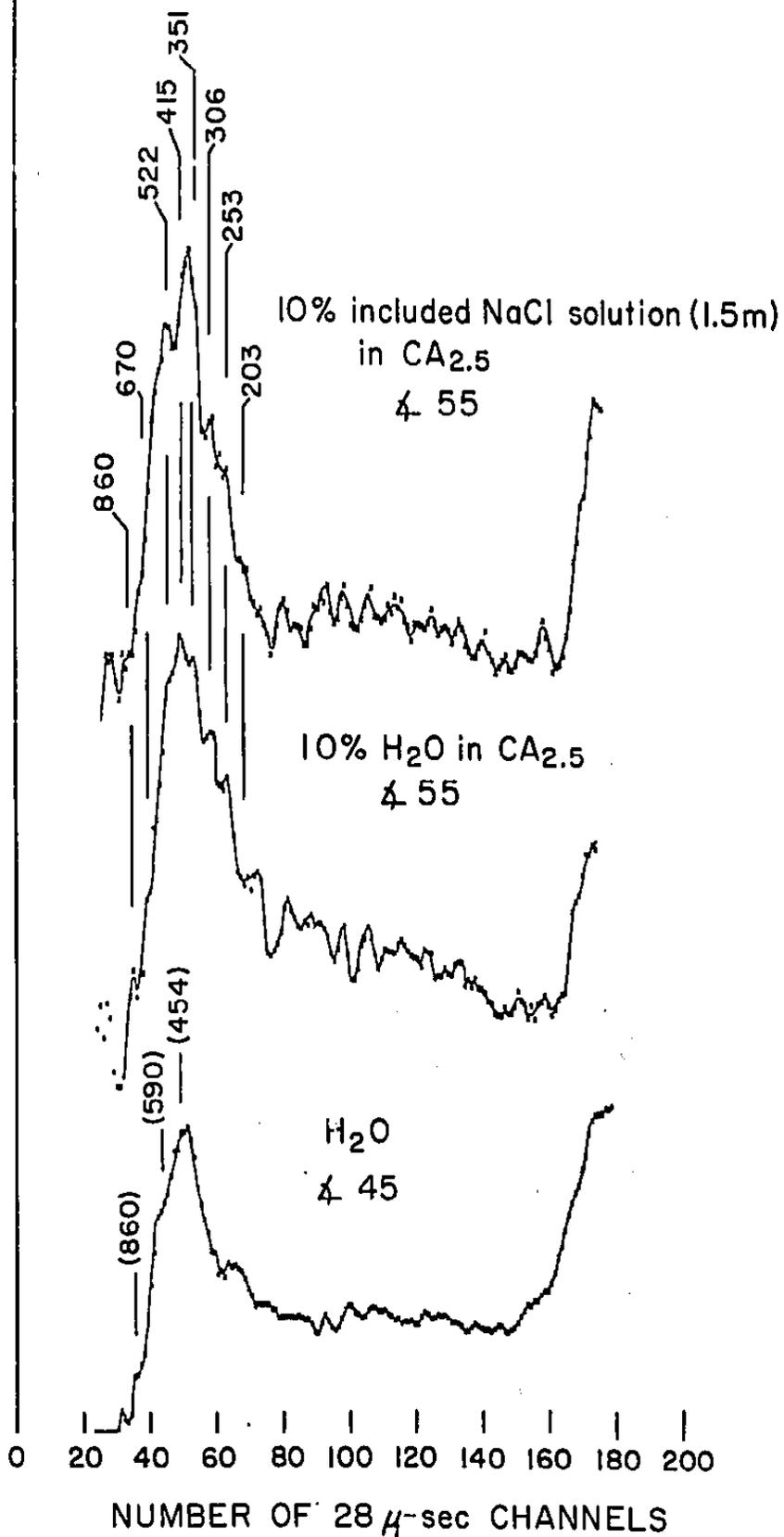
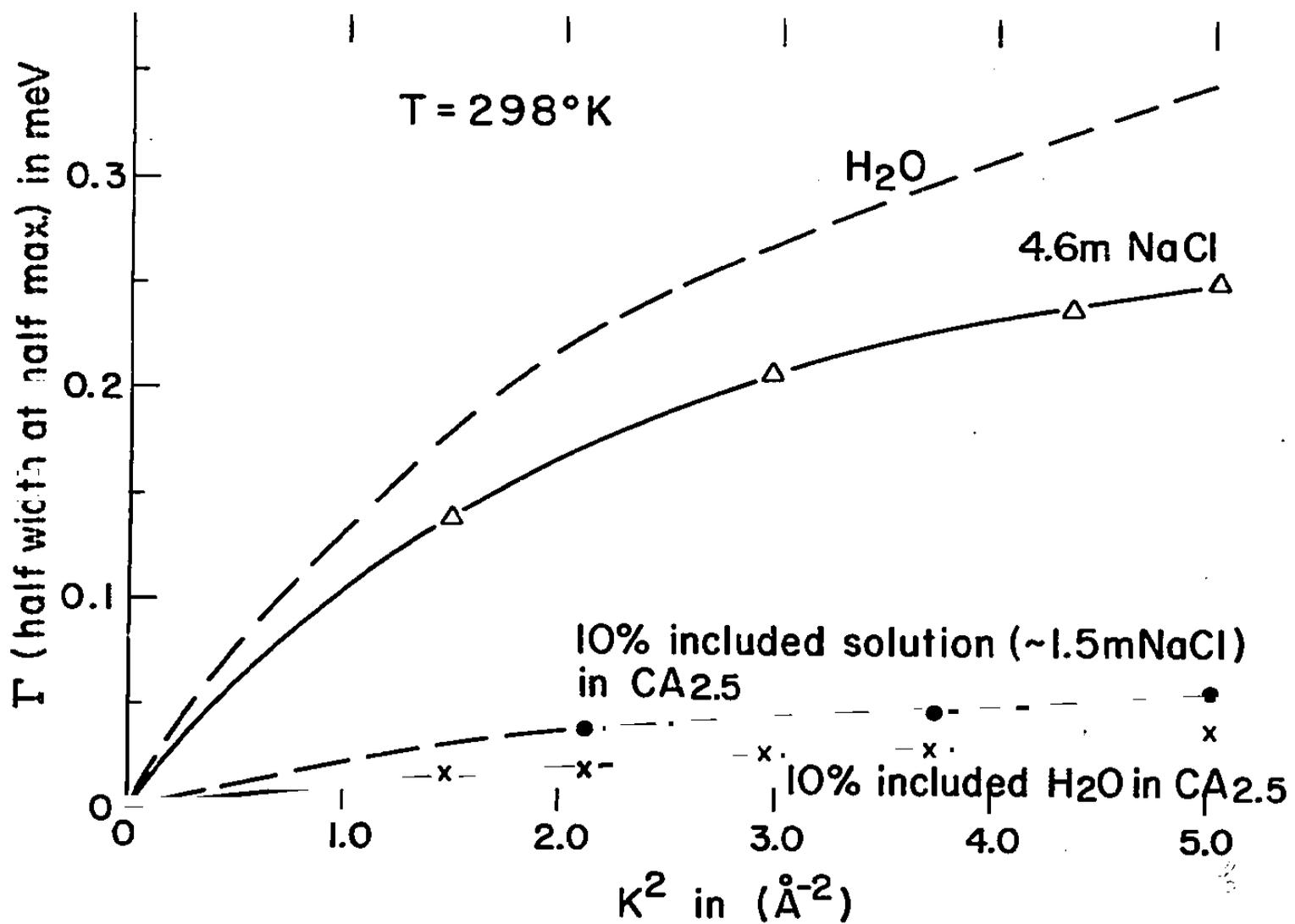


FIGURE 11

Curves of Γ vs. K^2 (corresponding to the solutions of Figure 10) are compared for

- (a) water at room temperature
- (b) a 4.6 m NaCl solution
- (c) an NaCl solution of an effective concentration of 1.5 m
- (d) 10 wt% in a $CA_{2.5}$ "dense layer" material

As discussed in the text, it should be noted that relative to pure water, a curve for 4.6 m NaCl solution lies lower, corresponding to a "structure-making" effect and, hence, a decrease in the self-diffusion coefficient, D , and an increase in the residence time, τ_0 . In contrast, the curve corresponding to a sodium chloride solution in a $CA_{2.5}$ membrane lies above the corresponding curves for the identical "dense layer" which contains only water which is a "structure-breaking" effect corresponding to an increase in D and decrease in τ_0 due to the inclusion of the NaCl in the membrane material. Hence, as detailed in the text, it appears that the sodium chloride has enhanced the equilibrium diffusion of H_2O molecules in the "dense layer" material.



47-3

FIGURE 12

The time-of-flight spectra for neutrons scattered inelastically from 5 wt% and 10 wt% water in CA_{2.5} membranes having an average molecular weight of 44,800 (cast from Eastman-398-10 cellulose acetate) and an average molecular weight of 35,100 (cast from Eastman 398-3) are compared.

INTENSITY IN ARBITRARY UNITS

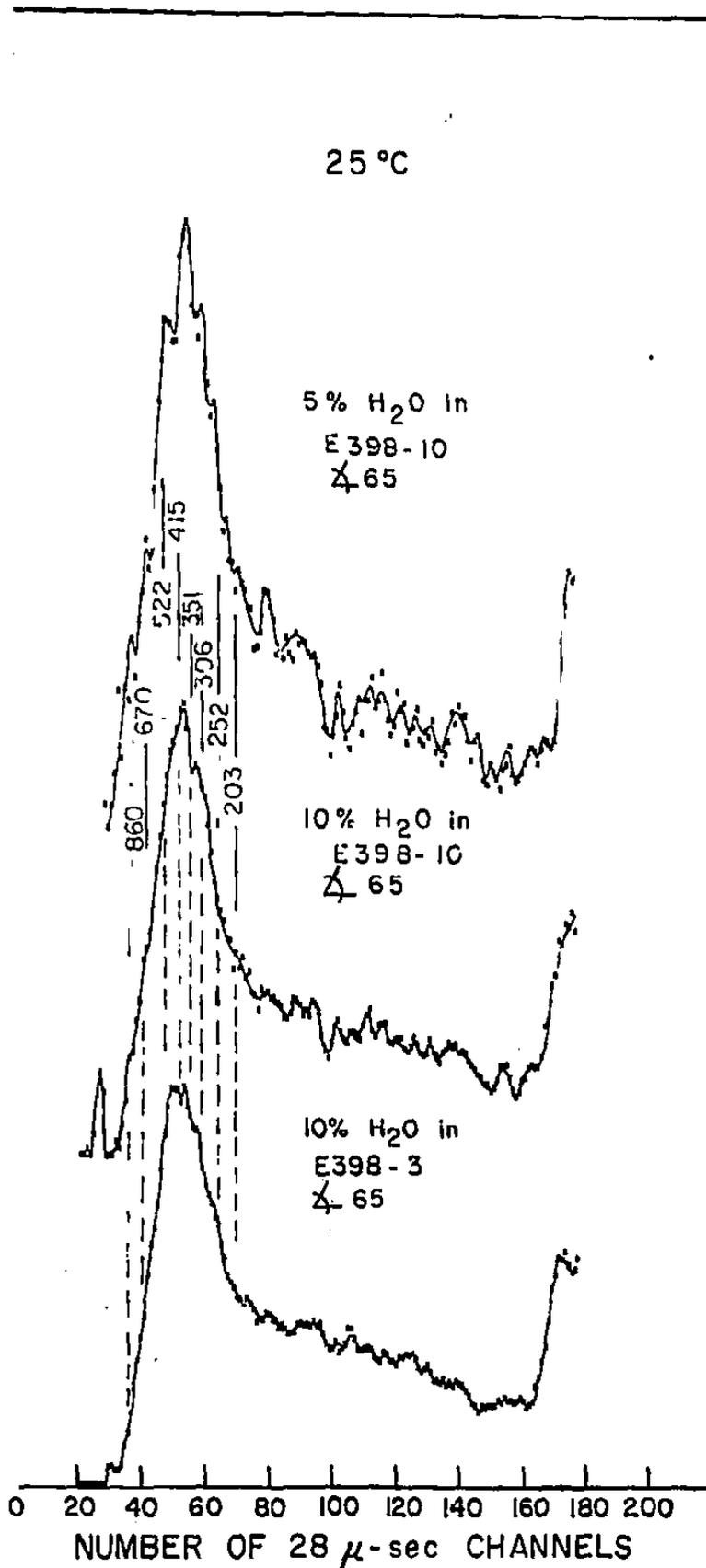
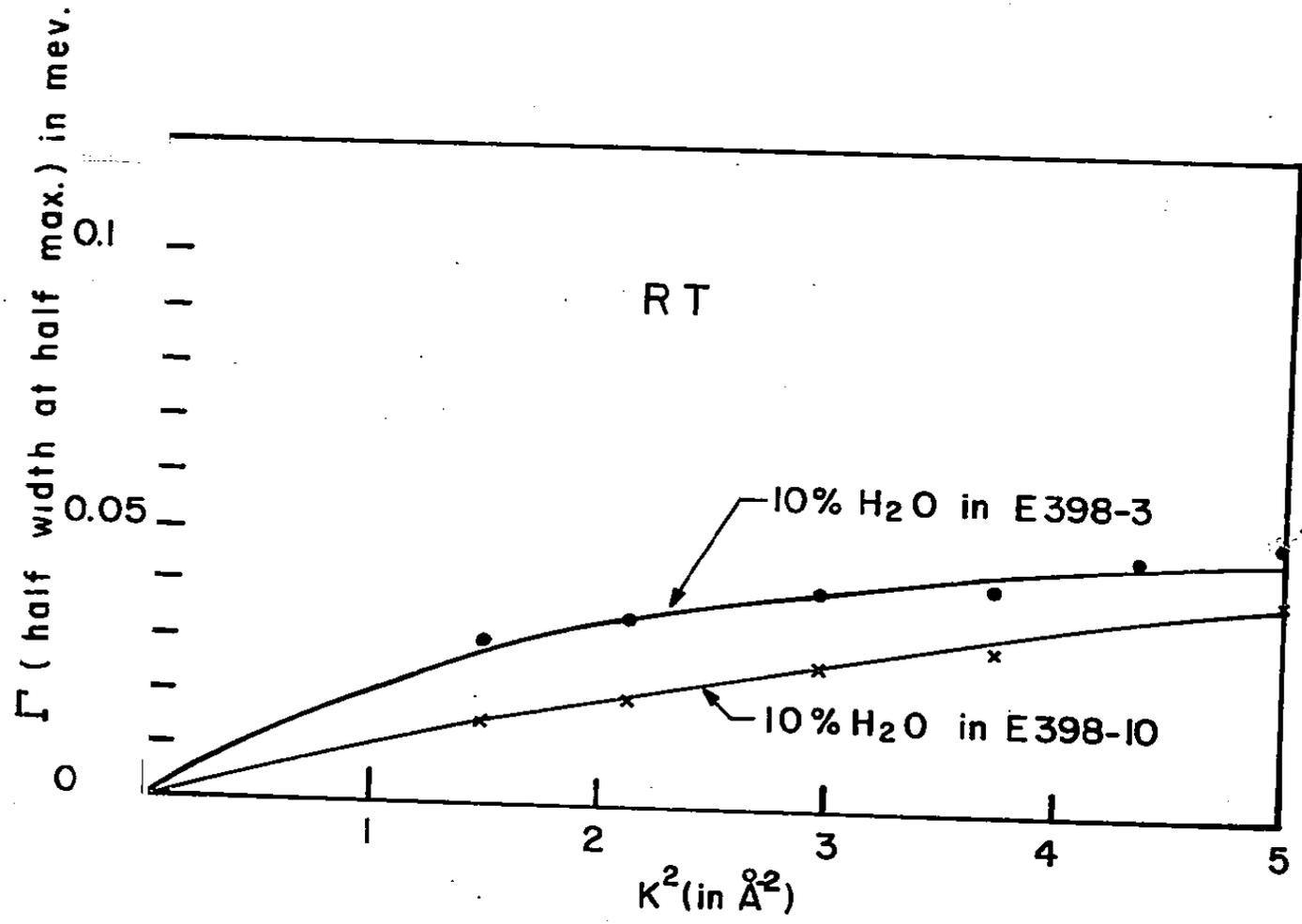


FIGURE 13

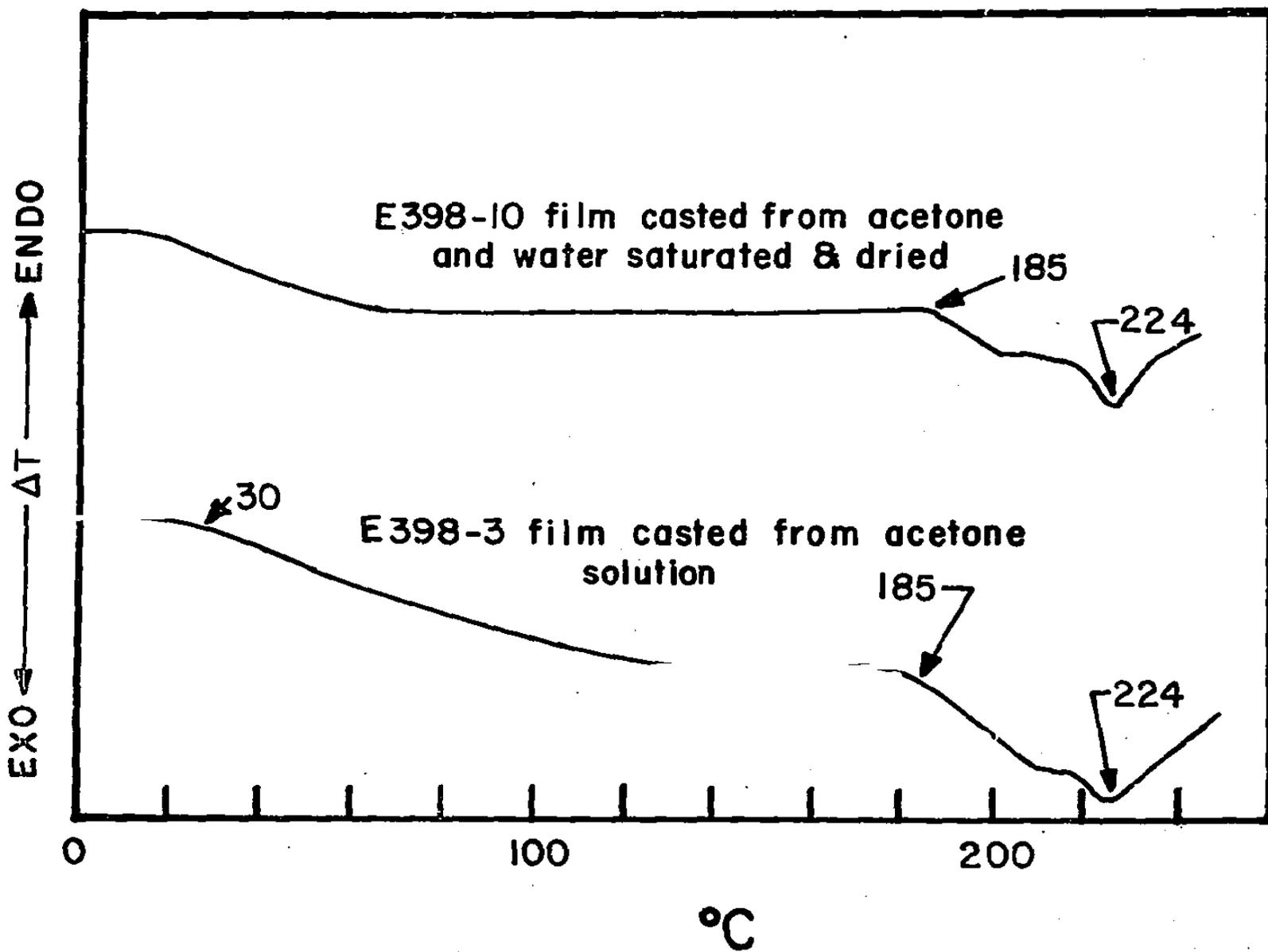
Curves of the Lorentzian half-width at half-maximum, Γ , of the diffusively broadened incident energy distributions as a function of the momentum transfer (K^2) are compared for 10 wt% water in the CA_{2.5} membranes having molecular weights of 44,800 (Eastman-398-10) and 35,100 (Eastman-398-3), respectively. It should be noted that the slope at the origin of these curves is proportional to hD and that at high values of K^2 the values of Γ approach h/τ_0 . Hence, the curve corresponding to the water in the lower molecular weight membrane appeared associated with a larger self-diffusion coefficient than that for the higher molecular weight material but nearly the same value of the residence time, τ_0 . As detailed in the text, this results from an increase in free volume with decreasing molecular weight that increases the self-diffusion coefficient but does not significantly alter the residence time, τ_0 .



49-b

FIGURE 14

The differential scanning calorimetry traces are shown for CA_{2.5} "dense layer" materials having average molecular weights of 44,800 and 35,100, respectively.



q-05

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