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THE STRUCTURE OF WATER-SWOLLEN POLY(VINYL ALCOHOL) AND THE SWELLING MECHANISM

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ABSTRACT

The swelling mechanism of poly(vinyl alcohol) (PVA) in a wide range of the equilibrium swelling index, of 7–153% (with H₂O) and of 12–297% (with D₂O), was investigated by IR, Raman, and broad-band NMR spectroscopy. Analysis of the spectral data obtained confirmed the presence of hydration water (bonded with polymer-free hydroxyl groups) and condensation water (not having been bonded with polymer hydroxyl groups) in poly(vinyl alcohol) swollen samples at low (~7%) and high (>23%) equilibrium swelling indexes, respectively. Moreover, it revealed the intra- and intermolecular hydrogen bonds breaking in the polymer swollen to higher extent (equilibrium swelling index > 85%).

INTRODUCTION

The structure of water-swollen poly(vinyl alcohol) (PVA) as well as the mechanism of swelling are of interest to a number of research cen-

ters. PVA is widely applied in the technology of films, fibers, and membranes [1-3].

The swelling of partially crystalline polymers by low molecular compounds has been studied previously. Some authors postulated that these compounds penetrate only amorphous polymer domains [4, 5]. Such a hypothesis, however, was questioned in the late 1970s when Iwamoto et al. [6] and Razumova et al. [7] found the amorphization of poly(vinyl alcohol) swollen with water. The former authors announced partial polymer amorphization whereas the latter ones concluded that all the polymer crystalline domains underwent full amorphization.

Two papers have been published [8, 9] regarding the swelling mechanism. Water which penetrated poly(vinyl alcohol) was postulated to be bonded to free polymer hydroxyl groups present in polymer amorphous domains and to crystallite surfaces (hydration water) as well as to form free water species domains between the polymer chain molecules (condensation water). The dependence relationship between the equilibrium swelling index and the extent of hydration and condensation water penetrating the poly(vinyl alcohol) has not been established.

The polymer samples investigated came from various sources, and they were distinguished by acetyl group content [10], tacticity [11], and crystallinity [12] as well as the mode of preparation, thermal treatment, humidity, etc. [13, 14]. Thus, the literature data concerning the swelling of PVA cannot be compared in order to describe the swelling phenomenon unambiguously.

In order to make a real approach to the swelling mechanism, in this work the present authors carry out a systematic study on PVA crystallinity changes within the swelling processes in terms of the hydration and condensation water content in a wide range of equilibrium swelling indexes. The preparation of polymer samples by using the same method and from the same source is considered to be of significance

EXPERIMENTAL

Materials

PVA was from Shin-Etsu A, Japan. It had a volatile matter content of 4.8 wt%, an ash content of 0.17%, and an acid number (mg KOH/g) of 0.42, a saponification number (mg KOH/g) of 8.61, an ester number (mg KOH/g) of 8.19, an alcoholysis degree calculated with respect to the ester number of 99.36 mol%, and a content of residual acetate groups of

polyvinyl acetate of 0.64 mol%. The average molecular weight, determined by the centrifugation method according to a procedure presented elsewhere [15], was $\bar{M}_w = 154,000$.

Dimethylsulfoxide (DMSO) (p.a.) was distilled under reduced pressure, dried over MgSO_4 , and redistilled. Acetone (p.a.) and methanol (p.a.) were dried over anhydrous MgSO_4 . Phosphorus pentoxide (p.a.), redistilled water, and heavy water (99.7% D_2O) were used.

Supersaturated aqueous solutions of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, KNO_3 , and $\text{K}_2\text{Cr}_2\text{O}_7$ were prepared in D_2O at 25°C .

Preparation of Samples

PVA films were prepared from 4% DMSO solutions and, for testing by Raman spectroscopy, from 4% aqueous solutions. After centrifugation, the solution was poured onto a flat glass plate. The solvent was evaporated at 40°C within 30 h. Then the film was removed from the plate and vacuum dried to constant weight at 50°C under a pressure of 3333 Pa (25 Tr) for 5 days and then for 3 days over P_2O_5 . The film thickness was measured with an Ultrameter A-52 apparatus (accuracy $\pm 3\%$).

PVA swollen samples (with H_2O and D_2O) were prepared by keeping PVA dried films (or PVA specimens which had been kept in water for 24 h) over supersaturated aqueous solutions of their respective salts or water at 25°C for ~ 2 weeks (until they had attained constant weight). Detailed swelling conditions are given in Table 1.

Procedure

Swelling measurements of the PVA samples with water (of 3–6 μm thickness) and D_2O (of 2.5–3 μm thickness) in the vapor and liquid phase were performed according to a procedure described elsewhere [16].

The mass of the samples was measured during swelling every 24 h with an accuracy of 0.00001 g.

IR spectra of dry and swollen samples, placed between two KRS-5 plates with silicone grease-sealed edges, were recorded against air in the range of 400–4000 cm^{-1} within 15 min by using a Perkin-Elmer type 155 spectrometer.

Raman spectra were obtained with a Coderg France model 165 spectrometer equipped with an argon laser beam of 448 μm wavelength and 200 mV power as a source of excitation. The scanning speed was 50 $\text{cm}/$

TABLE 1. Swelling of Poly(Vinyl Alcohol) (PVA) Films with H₂O and D₂O in the Vapor and Liquid Phases^a

Experiment	Salt	Swelling agent		
		H ₂ O		
		<i>H</i> in % ^b	<i>S_w</i> in % ^c	D ₂ O
1	Mg(NO ₃) ₂	52	7	12
2	SrCl ₂	70	12	31
3	(NH ₄) ₂ SO ₄	81	14	43
4	BaCl ₂ ^d	88	23	56
5	KNO ₃	92	28	65
6	K ₂ Cr ₂ O ₇	98	50	74
7		100	85	131
8		—	153	297

^aSwelling in the vapor phase over saturated solutions of different salts. Experiments 1–6: Over water or D₂O. Experiment 7: In the liquid phase. Experiment 8: At 25°C within 2 weeks [within 24 h and within 2 weeks with water (D₂O) vapor over water (D₂O) for the dripping].

^b*H* = relative humidity

^c*S_w* = equilibrium swelling index: g water/100 g dry polymer.

^dSwelling temperature: 24.5°C.

min. The spectral slit was 8 cm⁻¹. The scattering angle was 90°. The samples were placed in glass capillary tubes or between microscope plates with silicone grease-sealed edges. Before recording the spectra, the samples were directly illuminated by a laser beam (200 mV) for 10–30 min to quench the fluorescence that usually occurs during measurement.

¹H-NMR spectra were recorded within 20 min on a spectrometer constructed by the Institute of Nuclear Physics, Cracow, Poland (constant magnetic field in an autodyne oscillator coil producing oscillations of 17.455 MHz frequency, *H_m* = 30 mA, *H₁* = 18 μA, *R_c* = 35, lock-in amplification = 30, φ = 48°) using samples as narrow strips protected against moisture or water loss. All the samples used were of identical mass, density, and surface area in the dry state.

X-ray investigations were conducted on a Dron-1.5 diffractometer with CoK_α radiation equipped with a scintillation counter. The speed of the counter was 1°/min, and recording speed was 720 m/h. The initial

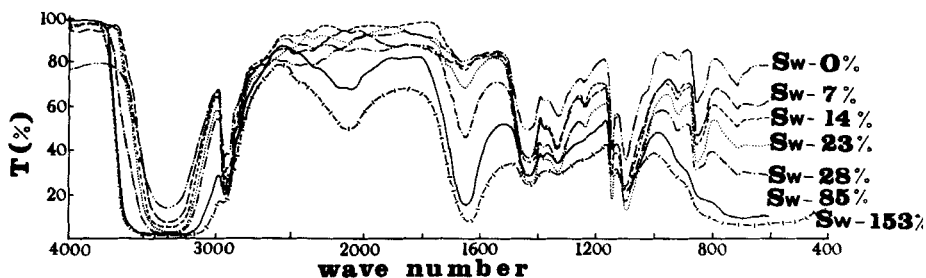


FIG. 1. Influence of equilibrium swelling index (S_w) on the changes in IR spectra of poly(vinyl alcohol) (PVA).

beam was formed by a 0.5-mm slot, and a 0.25-mm slot was placed in front of the counter. The lamp voltage was 36 kV, and the current was 10 mA. The radiograms were recorded in the angular range of 2θ ($2-40^\circ$).

Density measurements were carried out on a gradient column filled with a mixture of benzene and carbon tetrachloride. A new benzene-carbon tetrachloride mixture with an appropriate ratio was prepared for each sample series of a given swelling index. The column was calibrated prior to each use.

RESULTS AND DISCUSSION

IR spectra (transmission scale) of the samples swollen with H_2O are shown in Fig. 1.

As can be seen from Fig. 1, the intensity of the band at 3340 cm^{-1} increases with enhancement of the equilibrium swelling index. This can be explained by hydrogen bond formation between water and polymer hydroxyl groups (hydration water) and also between associated water droplets (condensation water), which is in agreement with previous literature data [8, 9, 17, 18]. Both of the above kinds of water species can hardly be distinguished in the 3340 cm^{-1} band. However, the present authors found a new band appearing at 2100 cm^{-1} in the IR spectrum (Fig. 1, $S_w = 23-153\%$) with an increasing amount of water in PVA. This new band was considered to be useful for the determination of condensed water. The band at 2100 cm^{-1} was reported [19] as originating from the associated water hydroxyl group. There was a lack of the 2100

cm^{-1} band in the spectra of dry PVA samples as well as in those swollen with a small amount of water until $\sim 23\%$ (Fig. 1, $S_w = 0\text{--}14\%$). Therefore, it is presumed that condensation water is present in swollen samples in the S_w range of $23\text{--}153\%$; its concentration in the polymer increases with an increase in the swelling index (Fig. 1, $S_w = 23\text{--}153\%$). On the basis of the above results, water penetrating the polymer is expected to be bonded with its hydroxyl groups (forming hydration water species). Increasing the amount of water penetrating the polymer results in the appearance of condensed water species.

There are also bands at 916 and 850 cm^{-1} in the IR spectra of the polymer swollen with water. These bands have not been unequivocally interpreted in the literature [20–25]. Some authors connect them with skeleton oscillations of syndio- and isotactic PVA chain units [20, 25]. In other papers [23, 24] they are assigned to the inter- and intramolecular hydrogen bonds in syndio- and isotactic polymer units, respectively.

It should be noted that in the IR spectra of PVA samples with a high swelling index, the bands at 916 and 850 cm^{-1} are broadened and overlapped. This can be due to the removal of polymer hydroxyl groups from intermolecular interactions between syndiotactic PVA chain units and from intramolecular interactions between isotactic units, respectively, and the formation of new hydrogen bonds between the polymer and the penetrating water. This may also allow the assignment of 916 and 850 cm^{-1} bands [23, 24]. Since the 916 cm^{-1} band has been observed to disappear at lower water concentrations (Fig. 1) it may be assigned to the intermolecular hydrogen bonds in the syndiotactic polymer chain units which are easily broken under the influence of water. Additional water of hydration appears in the polymer swollen with a large amount of water. The observed broadening and increasing in the intensity of the band at 3340 cm^{-1} with an increase in the amount of water in the polymer is probably also due to the above phenomenon (Fig. 1).

Analysis of spectra of PVA films swollen with D_2O vapor and liquid (Figs. 2 and 3) shows that the equilibrium swelling index is nearly identical, as exemplified by analogous changes in the bands at 3340 , 916 , and 850 cm^{-1} . These results confirm the proposed mechanism of PVA swelling. However, some differences are observed. Two new, closely spaced bands corresponding to O–D vibrations appear centered at 2480 cm^{-1} in spectra of D_2O vapor and heavy-water-swollen PVA samples. The intensity of the bands increases as the equilibrium swelling index increases. It should be noted that these bands begin to merge when the swelling index increases. These observations lead to a proposal that the

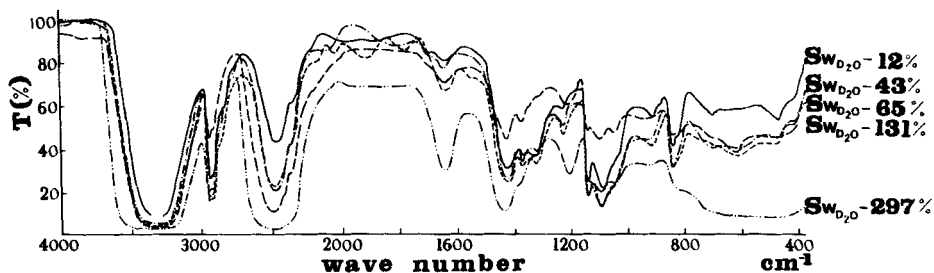


FIG. 2. IR spectra of PVA films swollen by D_2O vapors.

deuterated hydroxyl groups on a crystallite surface are more strongly bonded to the polymer at a smaller swelling index (Fig. 2, $S_w = 12, 43, 65\%$). Therefore, the largest splitting of the OD group band is observed in the spectrum of a sample with an equilibrium swelling index of 12% (Fig. 2). This assumes that the decrease in splitting of the band at 2480 cm^{-1} is not caused by an exchange of deuterium and hydrogen.

Another difference between the IR spectra of PVA swollen with water and heavy water may be found in the appearance of a new band at 1650 cm^{-1} . This is due to the formation of water by deuterium-hydrogen exchange as further evidenced by an increase in the width of the band at 3340 cm^{-1} .

The degree of deuteration was calculated according to Takadoro et al. [26] on the basis of the relative intensity decrease of the band at 3340



FIG. 3. IR spectra of PVA: nondeuterated (—), deuterated (— · —), and after substituting deuterium for hydrogen (— —).

cm^{-1} (Fig. 3). The band at 2940 cm^{-1} , originating from C—H vibrations and not subjected to visual changes during heavy water deuteration (Fig. 3), was considered as a reference band. The average deuteration degree was found to be 60%. It can be assumed that only the hydroxyl groups in the less ordered polymer domains underwent deuteration.

In contrast to IR investigations of PVA swelling, studies based on Raman spectroscopy revealed much less relevant information (Fig. 4). The swelling results in the superposition of crystalline bands at 1094 and 1147 cm^{-1} and of the amorphous band at 1124 cm^{-1} .

The swelling of PVA was also followed by $^1\text{H-NMR}$ studies. A home-built NMR wide line spectrometer was used at 17.455 MHz radio frequency (RF) for the study of protons in the PVA specimen. The spectrometer settings of the RF field, modulation field, amplification, etc. were kept constant for all measurements, so that the derivative line shapes would be comparable. The RF field amplitude was maintained well below the saturation limit.

The same amount of dry PVA exposed to different humidity conditions was sealed in glass NMR tubes to assure against loss of water. The use of narrow strips of PVA made sure that the weights, densities, and surface areas were the same for all the samples. Therefore, the conclusions drawn from a comparison of the NMR line shapes, discussed below, can be regarded as reliable. The area under the NMR absorption line is, in general, proportional to the number of resonance nuclei (protons in our case) in a sample.

The broad line is characteristic for immobile molecules while the narrow line shows up when highly mobile molecules exist in a sample.

The area under the NMR lines was calculated separately for narrow and wide components. After the first derivative of the absorption line was recorded in the experiment, two subsequent numerical integrations for each line were performed.

The ^1NMR spectra presented in Fig. 5 ($S_w = 7\%$) and Fig. 6 ($S_w = 85\%$) exhibit narrow and broad signals. The narrow signal can be attributed to protons weakly bound in slightly ordered polymer domains and from water penetrating these domains. The broad signal can be attributed to strongly bound protons of CH_2 , CH , and OH groups in highly ordered polymer domains as well as the presence of hydration water species. The assignment of these bands and their intensities are analogous to the work of Gupta [8].

Changes of the surface areas in the $^1\text{H-NMR}$ spectrum as a function of the equilibrium swelling index are shown in Fig. 7 and Table 2.

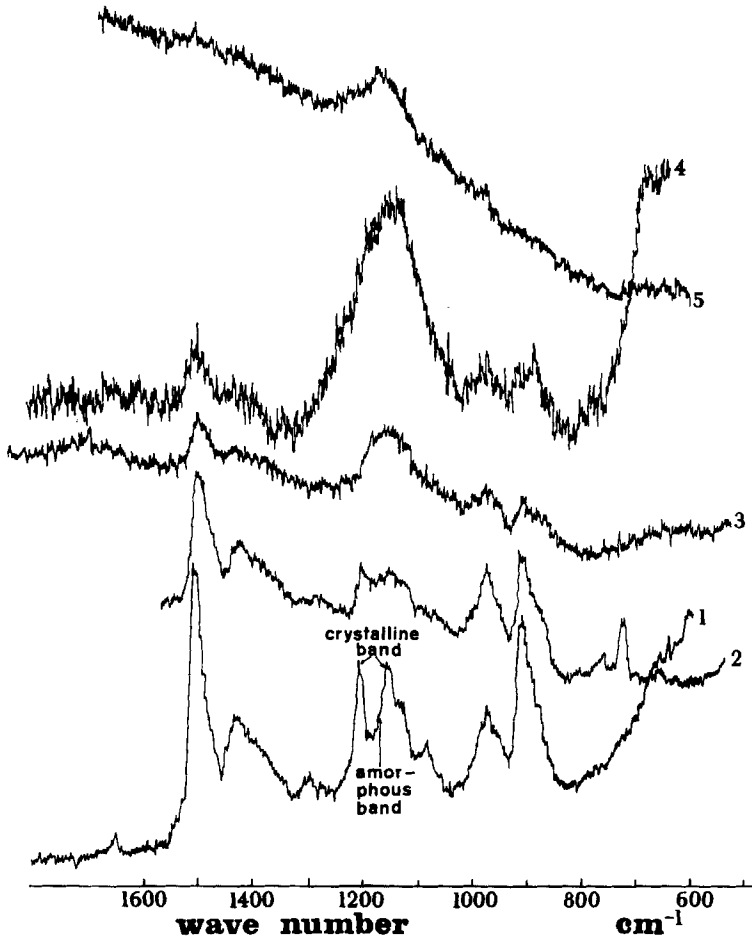


FIG. 4. Raman spectra of PVA: (1) powdered PVA; (2) dry films; (3, 4, 5) films swollen to an equilibrium state: in water $S_w = 460\%$, over water ($S_w = 140\%$), over a $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ solution ($S_w = 8\%$), respectively.

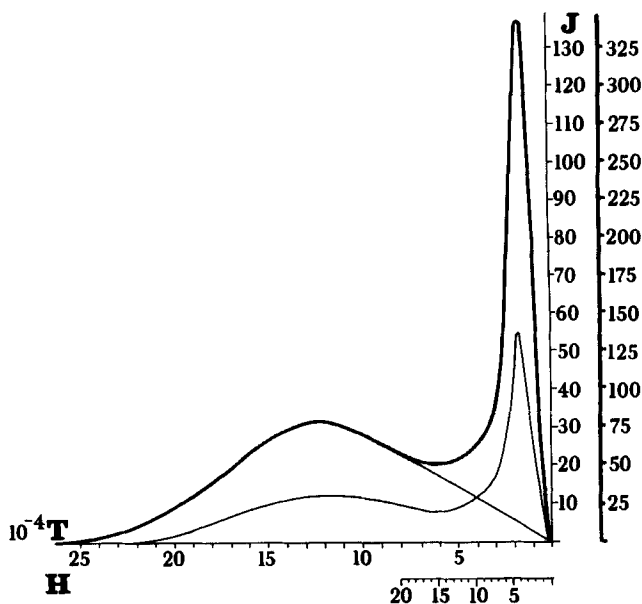


FIG. 5. Differential ^1H -NMR spectrum of PVA of 7 wt% swelling. Only one-half of the band is shown.

It can be seen from the data presented in Table 2 and Fig. 7 that the area under the narrow line increases over the entire swelling range, but the area under the broad line increases until S_w reaches 7% and then decreases. This indicates that water penetrates both the slightly and the highly ordered polymer domains within the whole swelling range. It should be mentioned that the above conclusion differs from that made by Gupta [8] who interpreted ^1H -NMR spectra as indicating that water penetrates only the amorphous domains.

The considerable increase in the area under the broad line in the spectrum of the sample of $S_w = 7\%$, when compared with that of the dry sample (Table 2), can be due to the stronger bonding of water with free polymer hydroxyl groups (probably situated on the crystallite surfaces). Again, it should be mentioned that Gupta [8], who observed an increase in the intensity of the broad signal in NMR spectra of PVA samples swollen in a low relative humidity (40%) medium, drew the same conclusion. The areas under the broad line in the NMR spectra of samples of $S_w = 50$ –153% (Table 2, Fig. 7) are smaller than they are in

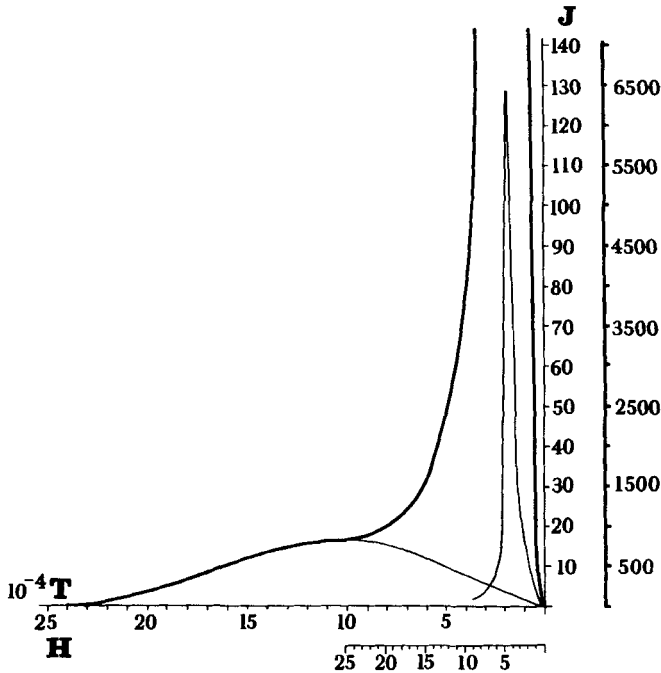


FIG. 6. Differential $^1\text{H-NMR}$ spectrum of PVA of 85 wt% swelling.

the dry polymer sample. It seems that in this swelling range the ordered polymer domains are being destroyed by penetrating water. The $^1\text{H-NMR}$ data presented above confirm the enhancement in proton lability with increasing water concentration in the swollen PVA which was observed previously by Mank et al. [9].

Results of x-ray studies on swollen PVA are presented in Figs. 8 and 9. The crystallinity of PVA was determined by using the height of the peak originating from the 101 (h_{101}) reflection measured from the maximum to the base line [7] with a 1-mm accuracy (Fig. 8). Heights of the h_{101} peaks are summarized in Table 3.

As shown in Figs. 8 and 9 and Table 3, the h_{101} peak height diminishes with an increase of the equilibrium swelling index. The changes in this height, however, are small within the range of $S_w = 7-85\%$, but for the dry sample and the one swollen with water these changes are considerable (Fig. 8, Table 3). This can be interpreted in terms of the PVA partial

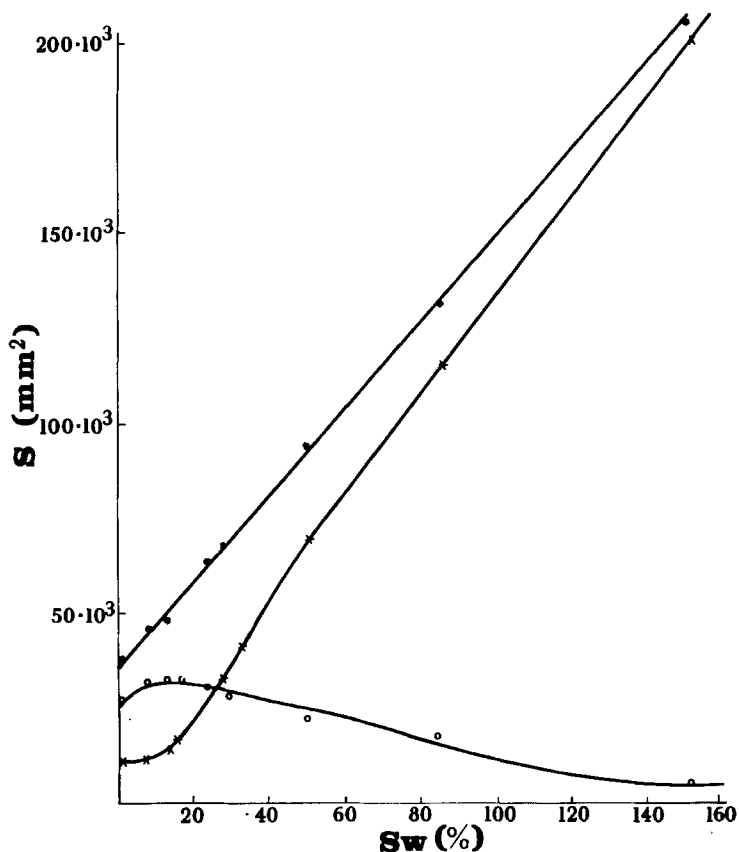


FIG. 7. Changes of the surface areas in the NMR spectrum as a function of the equilibrium swelling index (S_w).

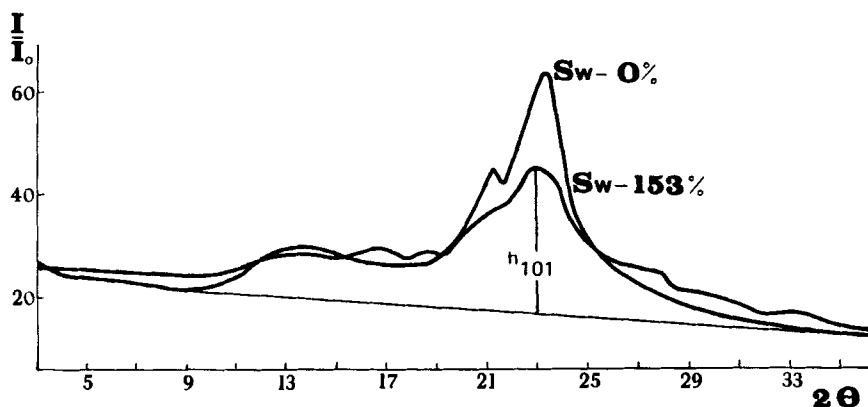
amorphization due to swelling, which agrees with the results obtained previously by Iwamoto et al. [6]. The full amorphization of PVA swollen with water, as reported by Razumova et al. [7], can be accomplished by simply placing the polymer in water.

The data obtained from densitometric measurements are summarized in Table 4. The degree of crystallinity in swollen PVA was calculated by a method published elsewhere [26]. The densities of both the crystalline and amorphous phases were obtained from the literature [26, 27]. The results show that the polymer density diminishes with an increasing equi-

TABLE 2. Areas Under the Narrow (S_n) and Broad (S_{br}) Signals in Differential NMR Spectra

Experiment	S_w , %	S_{br} , $m^2 \times 10^3$	S_n , $m^2 \times 10^3$	$S_{br} + S_n$, $m^2 \times 10^3$
1	0	26.732	11.225	37.957
2	7	32.830	12.434	45.254
3	12	32.482	14.518	47.000
4	14	31.300	16.737	48.037
5	23	30.444	33.555	64.000
6	28	28.542	41.352	69.894
7	50	22.668	72.892	95.550
8	85	18.542	115.678	134.220
9	153	7.452	202.433	209.885

librium swelling index, which is in agreement with literature data [28, 29]. The degree of crystallinity of the polymer is not influenced by swelling up to $S_w = 85\%$, but at $S_w = 153\%$ it decreases from 40 to 26% (decreases from $\sim 35\%$ crystallinity). These results are in accord with the x-ray results presented above. They show that water penetrates the amorphous phase up to $S_w = 85\%$ and the crystalline phase when S_w is of higher values (153%). Changes in the PVA crystallinity confirm some

FIG. 8. Dependence of the intensity I/I_0 on 2θ of the PVA film: dry and swollen in water.

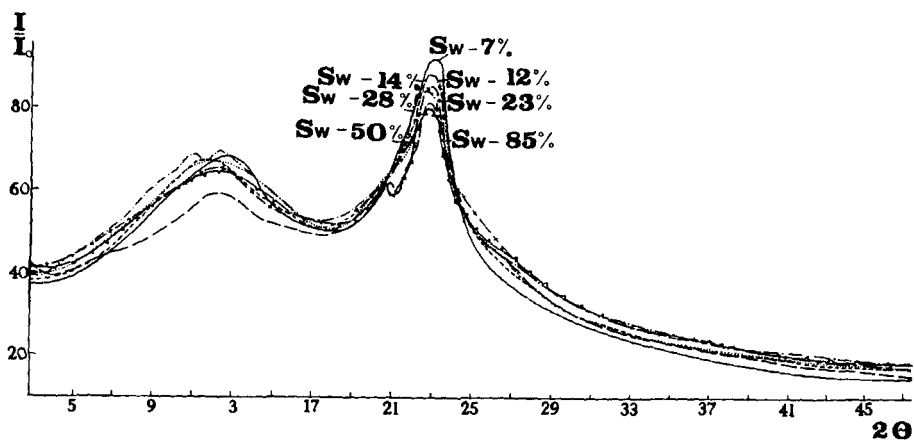


FIG. 9. Dependence of the intensity I/I_0 on 2θ of swollen films.

TABLE 3. Changes in the Height of the Peak Originating from Reflex 101 (h_{101})

Experiment	$S_w, \%$	h_{101}, cm	Series of measurement
1	0	56.5	I
2	7	22.6	II
3	12	21.7	II
4	14	21.6	II
5	23	21.0	II
6	28	21.0	II
7	50	20.4	II
8	85	19.6	II
9	153	39.0	I

TABLE 4. Densitometric Measurements of the Samples Studied

Experiment	S_w , %	$d \times 10^2$ kg/m ³	X , %
1	0	12.988	40.4
2	7	12.590	39.7
3	12	12.580	40.2
4	14	12.530	40.8
5	23	12.310	40.6
6	28	12.190	39.4
7	50	11.820	40.5
8	85	11.425	40.5
9	153	10.960	26.0

of the previous data from Takadoro et al. [28] and Iwamoto et al. [6], but the statement by Sakurada et al. [5] concerning water penetration into only PVA amorphous domains is not supported by our data.

CONCLUSIONS

Results obtained in this work allow the present authors to propose the PVA swelling mechanism as follows. Water, penetrating the polymer, forms hydrogen bonds with its hydroxyl groups, yielding hydration water species at a low swelling index (0–23%). The hydration water bonding is of two kinds: the stronger one involves hydroxyl groups located on the polymer crystallite surfaces, and the weaker one involves other available hydroxyl groups. Water that has not bonded with polymer hydroxyl groups forms a condensation water species; it appears in the polymer with an increase of the equilibrium swelling index (23–153%). This is accompanied by the continuous formation of hydration water. At large values of the equilibrium swelling index, 85% over water and 153% in water, intra- and intermolecular hydrogen bonds between polymer hydroxyl groups undergo a scission, and new hydrogen bonds between these groups and water are formed.

The swelling of PVA with water vapor does not cause any visible changes in its crystallinity, but the swelling in water results in a decrease in crystallinity (~35%). This is due to partial water penetration of the polymer crystalline phase.

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