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Transformations in the cellulose nitrate structure in the process of solvent vapor sorption

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SUMMARY

A technique permitting to record structure transformations in a polymer film by X-ray analysis directly in the process of low molecular weight solvent vapor sorption is developed. Applying it to cellulose nitrate (CN) - ethyl acetate (EA) system evidences the formation of a set of crystalline reflections in the initially amorphous film at a definite EA vapor activity ($p/p_s \approx 0.6$), the reflections disappearing after the removal of EA. The ordering of structure is associated with molecular complexes (MC) formation, MC being thermodynamically stable within a certain p/p_s range. It proves the validity of a qualitative phase diagram offered for CN - EA system (6). The peculiarities of MC formation and destruction are bound to assist in interpretation of sorption and diffusion properties of the system in question.

INTRODUCTION

The last ten years were marked by a notable success in the study of phase equilibria in polymer - low molecular weight substance systems. Quite a number of phase state diagrams were obtained experimentally and in the case of flexible -chain polymers they coincide fairly well with theoretical predictions (1,2). Discrepancies between experimental values and theoretical ones are somewhat larger in the systems based on rigid-chain polymers but still there is at least semi-qualitative agreement between them (3-5). At the same time for certain polymers systematic data concerning phase equilibria in the whole concentration range is not available. The important examples of this type are represented by systems based on cellulose and its derivatives. The situation can be accounted for by both a complex structure inherent to these polymers and its easy re-organisation effectuated by the presence of low molecular weight substances (6). The latter makes experimental data extremely difficult to interpret in terms of attributing it to some definite phase state, since the time scale characteristic of structure re-organisation and that of experiment differ, as a rule.

To understand the reasons underlying the observed changes in properties involving their irreproducibility one should have idea concerning equilibrium structure of solutions formed by such polymers. Consequently the study of the properties of such

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a binar system, with the solvent or plasticizer content changing, should be accompanied by the structure identification in the course of experiment by X-ray analysis.

Quite a few works carried out with this end in view mainly involved CN solutions. However they were not aimed to solve general problems. Thus in (7) additive compounds (MC) of CN with acetone and camphor, were proved to exist; in (8) structure transformations were studied during "forced" plasticization of CN with phthalic acid esters; the authors of (9) qualitatively recorded various types of transformations in the initially crystalline polymer structure under the influence of a number of solvents and plasticizers. All that refers to the glassy and rubbery state of CN.

In the range of fluid solutions CN forms liquid crystalline state with many solvents (10). So anisotropic solutions and MC are the main supramolecular structures in the systems based on cellulose derivatives. The hypothetic phase diagram for such a system was offered in (11). Basing on it, with available data from literature and own results taken into consideration, we reported a qualitative diagram for CN - EA system in a previous paper (6).

According to the diagram at issue MC structure is thermodynamically stable in a vast temperature-concentration range. Nevertheless it is the X-ray analysis that can directly prove their existence. So this contribution reports the technique developed for the simultaneous study of sorption-desorption isotherms in CN - EA system and direct identification by diffraction analysis of structures formed at certain portions of these isotherms.

EXPERIMENTAL

Sample preparation.

CN was obtained by nitration the cellulose sample with DP=400 and narrow MWD in a mixture of nitric and acetic acids according to (12). The nitrogen content is 13.3%. Films for sorption measurements (90-100 μm thick) were formed by slow evaporation of 0.5% EA solution at 20°C followed by prolonged leaching them in distilled water. Mass-thermal analysis estimates the residual solvent content not to exceed 0.1%. The initial films are evidenced as being amorphous by X-ray analysis.

Preliminary sorption studies.

Preliminary sorption measurements were fulfilled using conventional McBain vacuum balance at 20°C in the range of $p/p_s=0.2\div0.95$. The sequence of six sorption-desorption cycles was adopted, with the maximum p/p_s value successively increasing. The sixth cycle accomplished, the sample was equilibrated with EA vapor again at $p/p=0.87$ to measure desorption isotherm. Fig.1 shows the corresponding sorption and desorption isotherms.

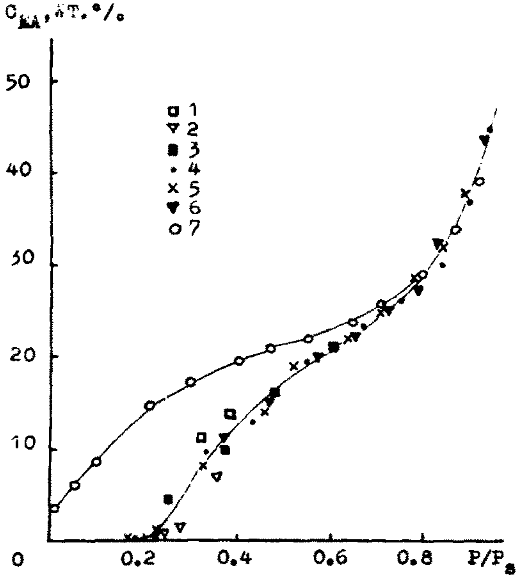

Fig.1 Sorption (1-6) and desorption (7) isotherms in CN - EA system at 20°C. 1-6 is the number of sorption cycle.

X-ray measurements.

X-ray diffraction patterns were recorded with a two-coordinate X-ray diffractometer KARD, its block diagram and main features being described at length in (13). The application of position-sensitive detectors to record diffraction patterns enables one to combine the sensitivity and accuracy usual for radiation counters with the simultaneous recording of a two-dimensional pattern inherent to photographic procedures. It allows to speed up diffraction experiments by more than an order of magnitude leading to entirely new possibilities involved in the investigation of relatively quick changes in structure of weekly scattering substances.

In Fig.2 there is a simplified block diagram of the instrument. The diffractometer is based on a flat two-coordinate multiwire proportional chamber with information readout from delay lines (14). Linear resolution is 1.5 mm in each coordinate, the number of spatial resolution elements is 256x256. The inlet detector window is 350x320 mm^2, the detection quantum efficiency of Cu K_α radiation ~70%. A diffraction picture is collected in a control SM-2 computer core memory. Software comprises a set of programs for any desired data processing by this or some other computer. Preliminary qualitative estimation of a diffraction pattern can be accomplished by visualizing it on a TV monitor screen with eight preset degrees in brightness. Fig.5 shows examples of such patterns.

To record X-ray scattering from samples undergoing sorption a special glass cell was constructed supplied with two Be windows for inlet and outlet of the incident beam and the scattered intensity. A block diagram of the cell is shown in Fig.3. The sample is placed into the cell vertically supported by a slide-type frame wherein a film can be inserted

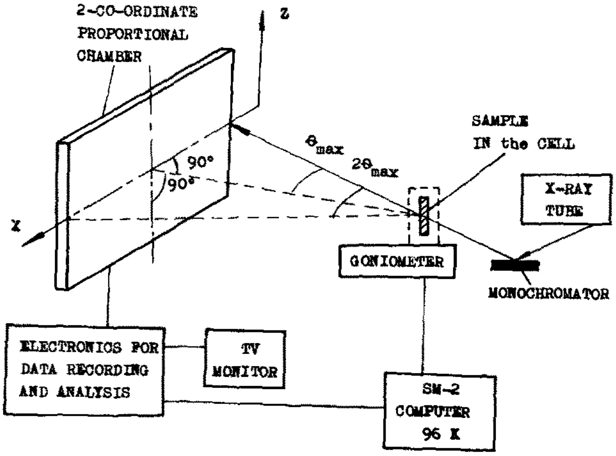

Fig.2 Simplified block diagram of a two-co-ordinate X-ray diffractometer KARD.

freely to let it swell spontaneously during sorption. The sample is thermostated by water circulating between double walls of the cell. The cell is covered with an air-tight ground in lid. The lid is connected with a pipe supplied with two vacuum taps to enable one independently to pump out the cell or the vapor source (after freezing the solvent

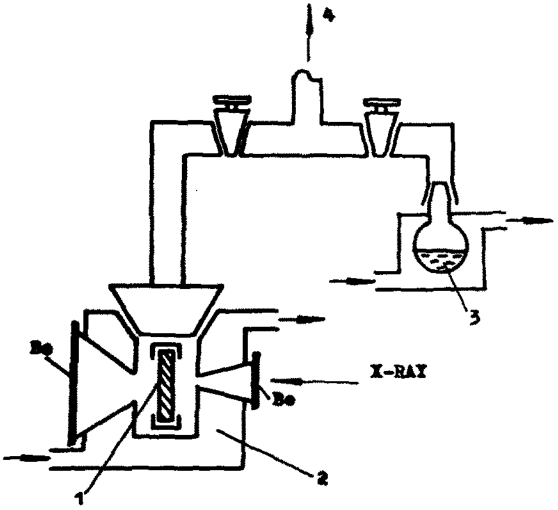

Fig.3 Experimental lay-out of a sorption devise permitting simultaneous record of X-ray diffraction pattern from the sample.
1 - sample;
2 - thermostated glass cell;
3 - thermostated vapor source;
4 - to a pump.

by liquid nitrogen) and to let the solvent vapor into the cell. Vapor source thermostated by a separate refrigerator is connected with the cell during the whole process of sorption. The dezired activity of a solvent vapor is achieved by varying the temperature of the source ($T_{source} < T_{cell}$).

The cell with the sample was mounted at a goniometer stage in a special holder which allows to adjust the sample in the center of the goniometer. The co-ordinate detector was aligned in such a way as to allow perpendicular drawn from its center to pass through the center of the sample to form with the primary beam the angle $\gamma = \theta_{max}$, where $2\theta_{max}$ is the maximum angle available for diffraction pattern detection. It implies that the primary beam hits a middle in height and extreme in length detector element. Such an experimental lay-out ensures both the best angular resolution possible for flat detectors and the maximum recorded range of diffraction angles 2θ, the sample-detector distance being fixed. The detector was not moved during measurements. Its position on the goniometer relative to the sample and the primary beam is known with accuracy permitting definition of the correlation between detector coordinates and the diffraction angle to be made. The sample-detector distance is 410 mm, angular resolution ~0.2°, the range of the recorded angles 2θ - 2-40° in the equatorial direction and -20-+20° in the meridional one. Cu K_α radiation from the sealed tube with 0.4x1.2 mm focus spot, monochromated by pyrolithic graphite crystal was used. The diameter of the collimator diaphragms was 0.8 mm. The data collection time was 500 s.

Data processing involved the introducing of corrections for the non-uniformity of the detector's characteristics over its surface, subtraction of the background scattering from the cell with solvent vapor but without the sample (recorded previously at various p/p_s), printing the intensities as histograms versus the angles 2θ. Since the diffraction patterns in the present case are axi-symmetric and necessary spatial resolution is lower than that of the diffractometer, the equatorial linear sections were recorded as the sum of intensities over three channels in horizontal direction and over eleven channels in vertical one.

p/p_s fixed, the course of reaching sorption equilibrium was judjed by kinetic sorption curves recorded with the same films using conventional McBain balance as described earlier. Another means to control the state of the system when recording X-ray scattering patterns was provided by measuring the total intensity over the chamber, its magnitude increasing until the equilibrium solvent concentration within the film was reached.

RESULTS AND DISCUSSION

Figures 4,5 show X-ray diffraction patterns chacteristic of certain portions of sorption isotherms after reaching equilibrium and of different desorption stages. The sequence of equatorial diffractograms modification is presented in Fig.4. The corresponding two-dimensional patterns, photographed from the TV monitor screen are shown in Fig.5. It can be seen that beginning with p/p_s=0.6 in the pattern of scattering from pre-

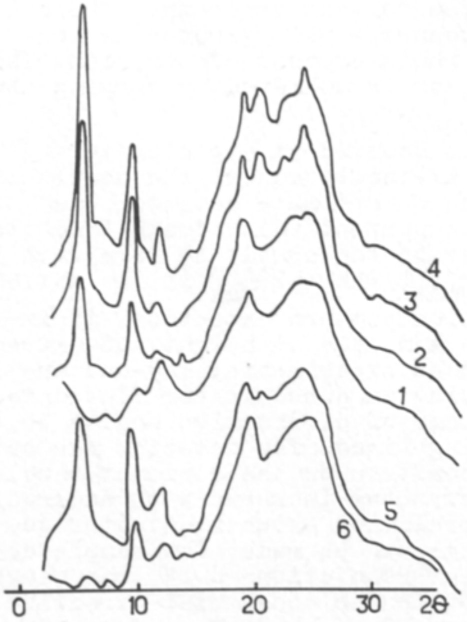

Fig.4

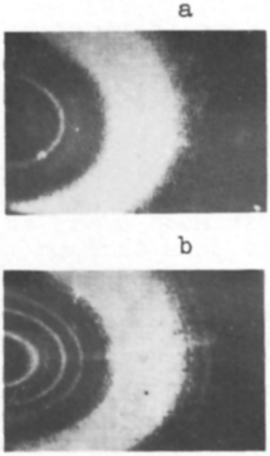

Fig.5

Fig.4 Diffractograms of CN film recorded during sorption (1-4) and desorption (5-6) stage. EA vapor activity p/p_s in the cell is 0(1); 0.6(2); 0.8(3); 0.95(4). Desorption time is 30 min.(5) and 3 days (6), with EA content in the film 10% and 3% correspondingly.

Fig.5 Diffraction patterns of the initial CN film (a) and the film saturated with EA at p/p_s=0.9 (b).

viously amorphous film there appear two intense crystalline reflections at angles 2θ 9.4° and 5.2° and several minor reflections at larger angles.

As p/p_s increases the intensity of crystalline reflections becomes somewhat higher relative to the level of amorphous scattering, the latter also increasing in the course of sorption. A slight decrease in the half-width of the two lines at issue is also worth noting.

The appearance of the crystalline reflections can be accounted for by the formation in the film at the definite p/p_s of additive compounds involving both the molecules of CN and EA in stoichiometric ratio. Such compounds - molecular complexes - are characterized by a long-range order and their sizes appear to grow a little as p/p_s increases. Fig.5 shows that there is no preferential orientation in the arrangement of MC throughout the film. Polymer fraction which takes part in the formation of MC is not large (10-20%) and seem to increase fairly little with p/p_s.

The diffraction patterns taken at the desorption stage help to understand the nature of sorption-desorption hysteresis observed at $p/p_s < 0.8$. It is worth noting that the form of the hysteresis is reproducible and it is not the result of capillary condensation. Preliminary sorption measurements evidence that after pumping EA for 30 min. from $p/p_s = 0.9$ its content in the film is lowered to 9-10%, the rate of EA diffusion from the sample slows down to a large degree and the whole process appears to become non-diffusion-controllable. The corresponding diffraction pattern is shown in Fig.4 (curve 5). The pattern changes very slowly with time, its shape suggesting the preservation of ordered enough formations in the film. After this sample had been exposed to air for three days ($p/p_s = 0$) which led to lowering the residual solvent content to 3-5%, it can be concluded that the sample practically resumed its initial structure.

We consider the observed sorption-desorption hysteresis to be of a relaxation-kinetics nature, the latter processes accompanying the formation and destruction of MC at the definite portions of the isotherm. The study of these phenomena is in progress now. It will assist both in making concentration position of various co-existing curves on a phase diagram more accurate and in comparing the isotherms with the concentration dependence of mutual diffusion coefficients in CN - EA system. These subjects will be discussed in separate papers.

In summary, the developed technique enables one to investigate the kinetics of structure reorganization in different regions of phase state diagram directly in the process of spontaneous formation of polymer solutions.

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