The polyacrylamide–water system: Application of differential calorimetry to study the mechanisms of dissolution

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Abstract

Differential heat effects and rates of H_2O sorption and desorption are investigated in the polyacrylamide (PAA)–water system at $0 < n < 25$ ($n = (H_2O)sorb/(-C(O)NH_2)$). It is stated that, at 292 K in air of 100% humidity, the equilibrium corresponds to $n \approx 18$ (n_{eq}); the heats of water-vapor sorption decrease from 56 kJ/mol (initial heat) to the heat of water vaporization (Q_L) at $n \approx 0.5$, and then they pass (up to n_{eq}) through several maxima and minima in the vicinity of Q_L; at $n > n_{eq}$ they are equal to Q_L. It is concluded that sorption of water by dry PAA leads to linearization of PAA molecules, to the space between the amido groups of each PAA molecule being filled with water, and to neighboring order at which each PAA molecule is surrounded (at the section normal to the main carbon chain) by six nearest ones. At equilibrium, the PAA molecules are separated from each other by a water layer of three-molecule thickness. © 1998 Elsevier Science B.V.

1. Introduction

Polyacrylamide (PAA) is a model polyamide to study questions of the polyamide behaviour in aqueous solutions. An interest to such questions is determined by the outstanding importance of polyamides in living matter and in industrial chemistry as well.

PAA dissolves in water. In standard conditions, integral heat of PAA dissolution in water is negative and small in magnitude [1,2]. PAA segments in dilute solutions shows preference to a contact with water rather than with other polymer segments [3,4]; direct intramolecular hydrogen-bonding of amido groups (AGs) does not occur extensively.

Differential heats of H_2O sorption by PAA are not to be found in the literature; detailed data on drying of PAA solutions are lacking. Partial filling of these gaps is the goal of our work.

Mechanisms of intermolecular interaction in the PAA–H_2O system, and also of transformation of this system under change of the PAA/H_2O ratio contain some white spots. Therefore, the essence of a number of data about this system remains an issue (e.g. [5]). The differential thermodynamic and kinetic data given below allow us to make an attempt to clarify some questions of the mechanisms.

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2. Experimental

2.1. Calorimeter

We used a FOSKA differential heat-conducting double microcalorimeter [6–8], with resistance thermometers as heat-flux sensors. Sensitivity in the negative or positive flux measurements was ca. 23 μW. A calorimetric ampoule, containing a solid or liquid sample, was (through a cylindrical canal) lowered down the calorimetric cell arranged within the massive thermostat.

Calorimetric fluxes were usually drawn to scale of ca. 3000 or 750 $\mu J/cm^2$ of a chart paper with an error of 0.7%. Sensitivity of the instrument allows measurements to be made to a scale of ca. 75 or 30 $\mu J/cm^2$ with an error of 1 or 2–3%, respectively. Therefore, we had a chance of high-accuracy controlling heat equilibrium before and after each experiment.

The calorimetric methods for sorption on monomers and for water sorption on polymers have been described in Refs. [9–11] and [12–14], respectively.

2.2. Glass apparatus and experimental procedures

The procedures were like the ones used to study the wetting and drying of the perfluorinated polymer Nafion [12–14].

A glass apparatus (Fig. 1) was used for experiments on vacuum drying of the PAA–H_2O system in the calorimeter and for pretreatment of the samples to be investigated.

An apparatus for calorimetric studies of water-vapour sorption and for pretreatment of the corresponding samples had the following differences from that in Fig. 1: the test tubes (3) had no necks (4); a magnetic cylinder covered with glass and also a thin-walled sealed glass sphere with a weight of distilled water were placed into each test tube; a known weight of powdered PAA was placed into the ampoule (1).

The desorption experiments in the calorimeter were organized as follows. Accurate PAA weights were placed into the ampoule (1). The weights of samples 3, 6, 7, 9, 10 and 11 were 0.128, 1.580, 1.243, 0.316, 0.401 and 0.376 g, respectively. The mass of dry PAA in a particular sample was calculated on the basis of preliminary experiments with PAA on its vacuum thermodrying (see below). An accurate weight of distilled water was added into the ampoule, and the tube (5) of the apparatus (Fig. 1) was sealed to a vacuum set. Before the experiments, the samples of the PAA–H_2O system were held, having regard to the data of [5] on "the instability effects", namely they were held for (days): 15 (sample 3), 30 (sample 6), 8 (sample 7, before the rate (Fig. 4) experiments), 14 (sample 7, before the heat (Fig. 3) experiments), 6
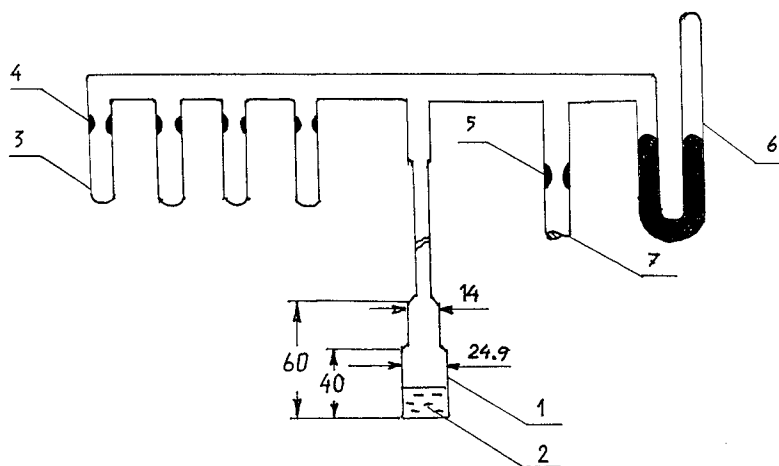

Fig. 1. Glass apparatus to study water-vapour desorption (sizes are given in mm): (1) ampoule; (2) sample; (3) test tube for freezing out the water; (4) neck; (5) neck between the apparatus and vacuum set; (6) mercury manometer; and (7) tube to vacuum set.

(sample 9, before experiments 1–6), 9 (sample 9, before experiments 7–14) (Figs. 3 and 4), 6 (sample 10), and 16 (sample 11). Then, an ampoule was out-gassed in the frozen state at 77 K for some minutes up to 1 Pa, heated up to room temperature, and repeatedly out-gassed in the frozen state. Following that, the apparatus was sealed under vacuum across the neck (5), and the ampoule (1) was lowered into the calorimeter.

Desorption was performed by ration freezing out the water from the ampoule (1) into the test tubes (3), subsequent sealing off the test tubes one by one across the necks (4), and exact weighing the desorbed water as the difference in mass of a sealed test tube with water and the same test tube but cut in two and well dried. The heat equilibrium was established before and after each experiment.

Duration of each desorption experiment was usually chosen such that the desorbed quantity was 50–150 mg. At $n>2$, it was from 2–3 up to 8–10 min, depending on the rate of desorption (n being the number of sorbed H_2O molecules per one amido group of the weight of PAA; $n=1$ corresponds to 0.253 g of H_2O per gram of PAA). After sealing off any test tube (3), containing a little water, the heat equilibrium was reached almost as quickly as after instantaneous turning off a calibration electric heat effect. At $n<2$, each desorption was continued for 20–40 min or longer, but after a test tube was sealed off, the heat equilibrium was reached as quickly as at $n>2$.

Calorimetric experiments on sorption were organized as follows. A PAA weight (1.836 g, sample 8) in the ampoule (1) of the apparatus for sorption was dried under vacuum for 4 h at 373 K. In the course of drying, no gases or vapours were desorbed other than water vapour. Such a treatment is sufficient for complete nondestructive drying of PAA. Desorbed water was weighed. By this means, the weight of dry PAA was determined. Then, the apparatus was sealed under vacuum across the neck (5), and the ampoule was lowered into the calorimeter.

The experiments were performed through ration sorption of water weights vaporizing from the glass spheres being broken (outside the calorimeter) one by one with a magnetic cylinder via an outside magnet. Each regular sphere with water was broken after the thermodynamic equilibrium, that had been destroyed by sorption of the preceding ration, was established. The water rations were, as a rule, 15–25 mg. After a

glass sphere was broken, the water droplets were of so large a radius of curvature that the vapour pressure in the absence of a water-absorbing agent comprised ca. 80% of the equilibrium vapour pressure over the plain H_2O surface. Completeness of H_2O sorption from each ration was controlled by the manometer (6). Termination of a heat process was controlled by the thermokinetic curve. The experiments were finished when the rate of sorption became too low for the heat effect to be measured. Up to this moment, the vapour pressure in the apparatus was near the pressure in the absence of a water-absorbing agent.

Water-vapour sorption by two weights of PAA, 1.5705 (sample 4) and 0.2117 g (sample 5), from air of 100% humidity was measured at 298 K. Weight glasses with the samples were placed inside a firmly closed desiccator. The desiccator contained a vessel filled with water.

Preliminary experiments were performed with samples 1 and 2.

The random error in the mass of sorbed (desorbed) water was 0.5%, and that in the molar heat effects was 0.70%. The absolute error, (Δn), in calculated n values in a sample before desorption experiments, was estimated as 0.20 ± 0.05. It is determined by the irregularity of amido groups in the polymer and by the error in preliminary experiments on H_2O concentration in PAA under room conditions. As the experiments on desorption are performed, the error in n values increases and can achieve values as high as $\Delta n=0.4$ at $n=1$. A regular error cannot always be exactly estimated. In this work, we found a possibility to estimate the regular error in the differential heats of desorption as 1.13% [15], and cleaned the results of Fig. 3 from them.

2.3. Material

PAA was used as a powder, grain size <63 μm, or as a solution in distilled water. The polymer had the molecular mass of $(3–5)\times10^6$ and contained one Na atom per 20–30 structural units.

3. Results

Preliminary experiments led us to the following conclusions. In a room with air of 80% humidity,

PAA contains ca. 100 mg H_2O/g ($n=0.4$), and it can be fully dried by 4 h vacuum heating at ca. 358 K, about two-thirds of water being desorbed (up to $n\approx0.13$) under vacuum at room temperature. Increasing the desorption temperature up to 378 K hastens drying of the polymer, but does not enhance the total quantity of desorbed water. Dry PAA sorbs water vapours from humid air of the room very slowly. For instance, in 185 h it sorbs only 25% of the water quantity desorbed in the process of drying. During the initial 7.5 h, and the subsequent 178 h, the same quantity of H_2O was sorbed. Evidently, this means that a rate of sorption on a solid sample is limited by water-vapour diffusion in air to the surface of a sample.

Water-vapour sorption from an air-free volume proceeds much faster than from humid air. For example, the quantity of water sorbed for 1.5 h from the air-free volume was greater than the quantity of water sorbed for 185 h from the room air. Under conditions of sorption experiments in the calorimeter, the rate quickly decreased from one experiment to another. A rate of sorption is limited by the surface process, but not by diffusion in the body of PAA. This is evident from the fact that a prolonged exposition of a sample under vacuum (after any sorption experiment) does not lead to the subsequent increase in the rate of sorption. At sorption from $n=0.24$ up to $n=0.38$, the evolution of heat lasted as long as 18 h. Therefore, further sorption experiments were impossible. On the other hand, the rate of desorption decreases progressively with decreasing n values, and at $n<0.5$ it becomes too slow to be measured exactly. Therefore, in an air-free medium, we had a chance of measuring the rates and heats of water desorption or sorption at $n>0.5$ or $n<0.5$, respectively.

Over the PAA–H_2O system, containing 4.5 g H_2O/g PAA (i.e. at $n=18$), a drop in the equilibrium water vapour pressure as against the equilibrium pressure over pure liquid water, if any, is within 1–2 hPa. Thus, in an air-free medium and at $n>18$, we had the chance to measure rates and heats of desorption only at a room temperature somewhat higher than
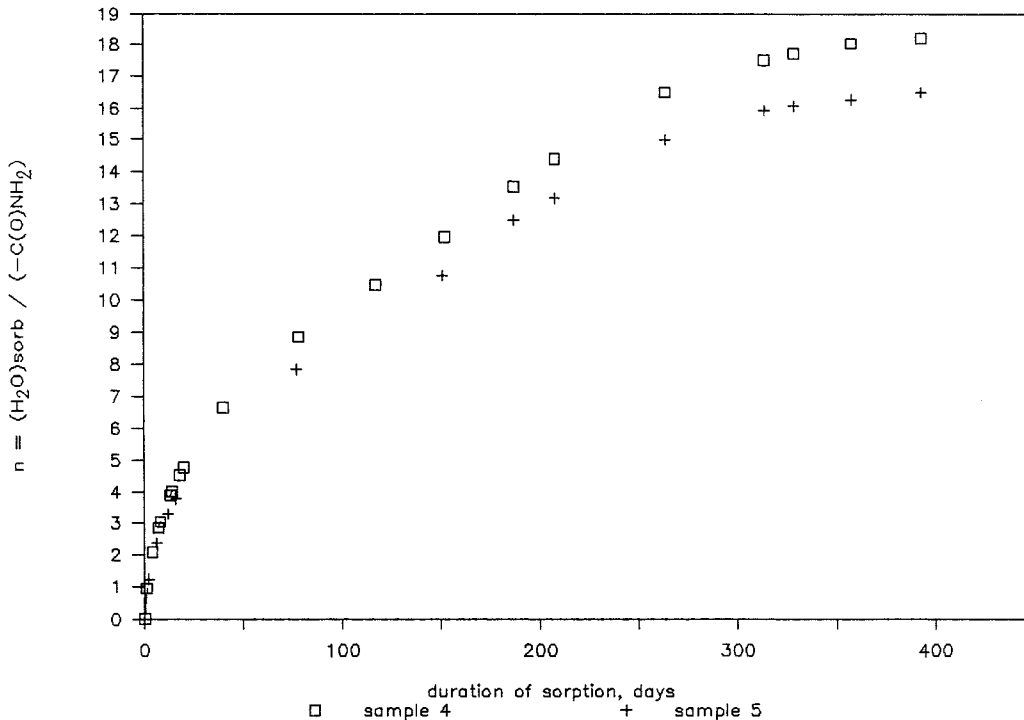

Fig. 2. Dependence of degree of wetting of the polymer on duration of sorption in air of 100% humidity (samples: 4 and 5).
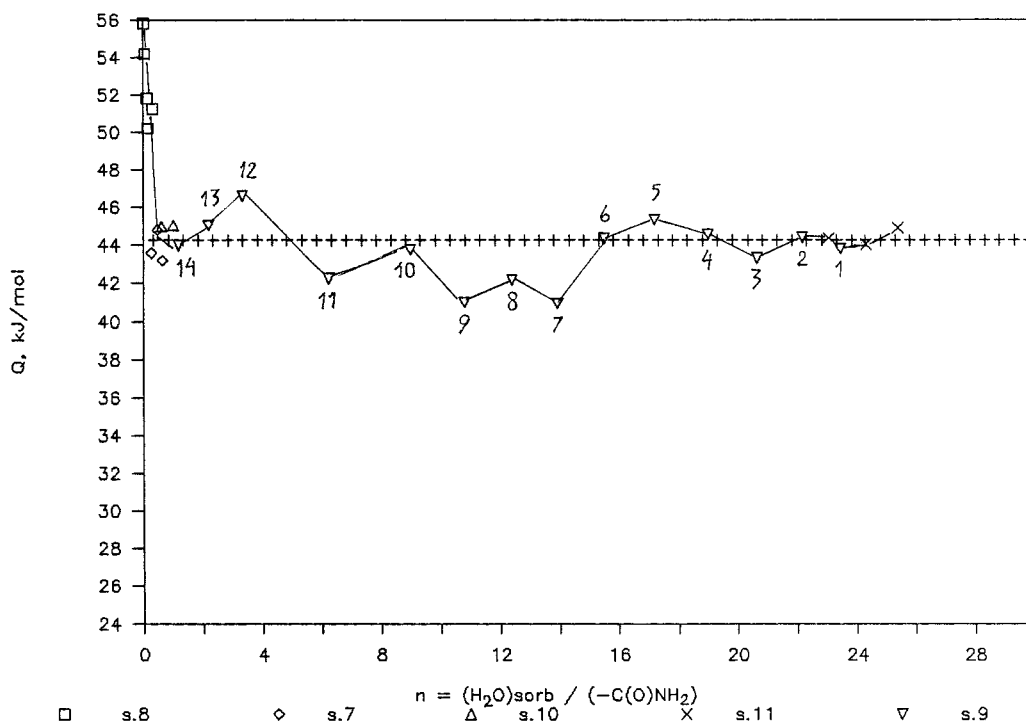
Fig. 3. Dependence of differential heats of water-vapour sorption on degree of wetting of the polymer (samples: 8 (sorption experiments); 7, 9, 10 and 11 (desorption experiments)).

the temperature inside the calorimeter. Otherwise, water evaporates spontaneously from the PAA–H_2O system and condenses within the necks (see (4), Fig. 1) and also within other narrow parts of the glass apparatus.

Results of water-vapour sorption by PAA in air of 100% humidity are given in Fig. 2. PAA sorbs the equilibrium quantity of water (n_{eq}) for ca. 13 months, n_{eq}=17–18. If the PAA–H_2O system contains more than 18 molecules of H_2O per 1 AG, the superequilibrium water is an inert diluent. Atmospheric air retards desorption, blocking diffusion of the superequilibrium water outwards from the surface.

Fig. 3 gives equilibrium differential molar heats of water vapour sorption. The sorption–desorption process is reversible. Therefore, the results of sorption (sample 8) and desorption (samples 7, 9, 10 and 11) experiments are shown in one plot, the values opposite in sign to the measured heats of desorption being plotted. The dashed line corresponds to the equili-

brium heat of water-vapour condensation, Q_L. It is clear that the sequences of sorption or desorption experiments correspond to motion along the abscissa of Fig. 3 from left to right or from right to left, respectively. To make further discussion more convenient, the experimental points measured on sample 9 (14 experiments) are listed in Fig. 3 from right to left in the sequence of their performance.

Differential heats of desorption were reproduced on 3 samples and on 2 samples within the intervals 0.5<n<3 and 22<n<26, respectively. The standard deviation was 0.7% only, as in the calibration experiments. Fig. 3 shows the maxima at ca. n=0, 4, 8 and 12, the minima at ca. n=6, 10 and 14, and also constant (near Q_L) heats at n>n_{eq}. The heights of the extrema are larger than the standard deviation (0.31 kJ/mol) by a factor of several units.

In the bulk of PAA–water system, the process of inception of minute vacuum bubbles, the bubble growth, and their merging into a big bottle-like bubble was observed during water desorption in the air-free
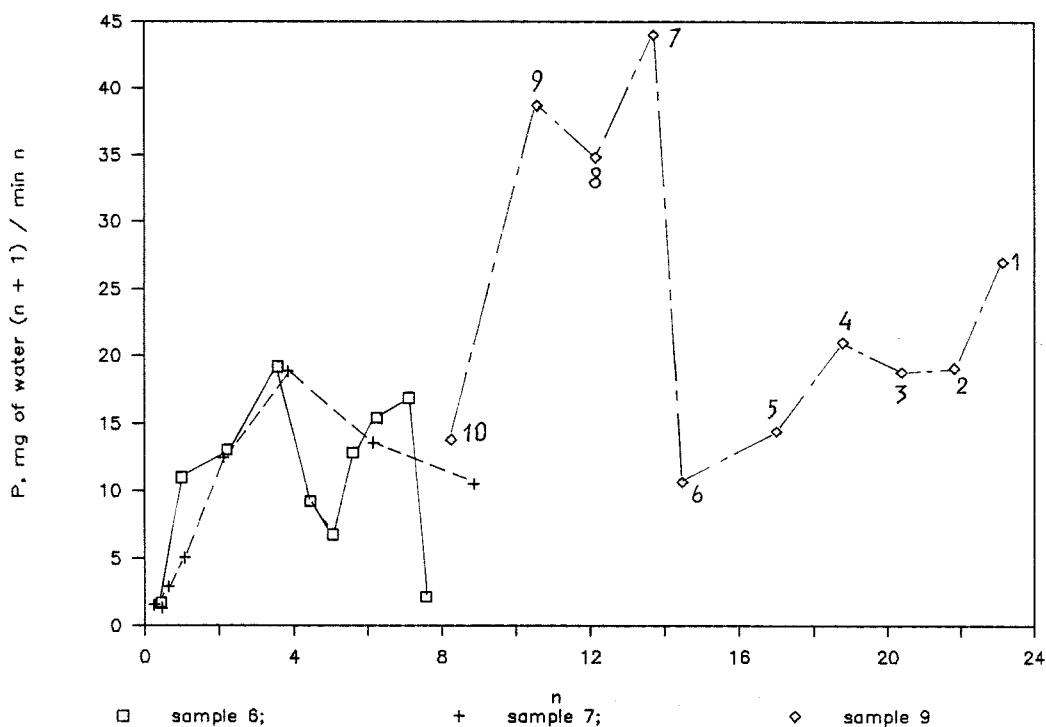
Fig. 4. Dependence of probability of desorption on degree of wetting (samples 6, 7 and 9).

medium. This phenomenon is of importance in consideration of the mechanisms of intermolecular interaction in the PAA–H_2O system.

Fig. 4 gives the n-dependence of the value proportional to the probability of desorption (below it is termed as "probability of desorption" (P)) of each sorbed molecule.

Under conditions of our desorption experiments, the water pressure over a sample was much less than the equilibrium one. Therefore, it may be approximately deduced that, in the course of each desorption experiment, the rate of sorption is negligible as compared with the rate of desorption.

Rate of desorption from the PAA–H_2O system can be limited by diffusion within the volume or by evaporation from the solution surface, depending on parameters of the process. When several samples of the same H_2O concentration are considered, the rate of desorption must be proportional to the volume or to the solution surface area in the first or second case, respectively. In our desorption experiments, the same calorimetric ampoule was used for all the samples. Let

the samples of different volume be characterized by the same H_2O/PAA ratio. Thus, at a rate of water desorption limited by evaporation from the solution surface, the rates of desorption from such samples should be equal in value. But, it is not an easy task to clarify the essence of the limiting process on the background of abrupt rate changes under changes of the n value. The point remains that the rates of desorption from two samples under comparison must be measured over the same narrow n-range. This circumstance (and also the desire to reveal sharply the n-values at which a rate takes the maxima and minima values) brings us to minimize the time of water desorption in each experiment in order to minimize the desorbed mass, i.e. Δn values. However, minimization of time contradicts the necessity to measure the time of desorption to a high accuracy. The best fulfilment of the contradictory requirements about the smallness of Δn values and a high accuracy was achieved in the experiments on sample 6.

The volumes of samples 6, 7 and 8 are in the ratio of 1.28 : 1.00 : 2.54. But, in the experiments performed

on different samples at much the same n values, the rates differed in many cases by a factor of 1.05–1.15 only. For instance, in the experiments on samples 6 and 7, the following rates of water desorption (mg/min) were measured: 13.3 and 11.6 (at n=6.25 and 6.16, respectively), 14.5 and 15.05 (at n=3.57 and 3.85), 9.0 and 8.5 (at n=2.21 and 2.11); on samples 7 and 9 these were: 9.5 and 12.3 (at n=8.85 and 8.2). Taking into account the fact that the rates are averaged over some n-ranges, the results under consideration provide reason enough to believe that the rate (r) of water desorption is limited by water evaporation from the solution surface rather than by a volume process. A high rate of reaching the heat equilibrium, after any desorption experiment is finished (see Section 2.2), testifies this conclusion.

Then we have

$$r = -\Delta N/\Delta t \equiv WcS, \tag{1}$$

where $\Delta N/\Delta t$ is the number of H_2O molecules desorbed in unit time from the solution surface area S at the surface H_2O concentration c, and W is the probability for each molecule to be desorbed during unit time. Let us assume that the surface comprises AGs and H_2O molecules, and that

$$c = n_{H_2O}/(n_{H_2O} + n_{AG}) \equiv 1/(1 + n_{AG}/n_{H_2O}), \tag{2}$$

where n_{H_2O} and n_{AG} are the numbers of H_2O molecules and of AGs on unit surface, respectively. Also, assume that

$$n_{AG}/n_{H_2O} = 1/n. \tag{3}$$

Then,

$$c = n/(n + 1) \tag{4}$$

and

$$r = WSn/(n + 1). \tag{5}$$

Considering that S=const with n, we have

$$r = Pn/(n + 1). \tag{6}$$

From Eq. (6), we finally obtain

$$P = r(n + 1)/n. \tag{7}$$

Fig. 4 shows that P does not vary smoothly with wetting; in turn, it passes through the reproduced n-ranges characterized by the higher or lower prob-

abilities of desorption. When $n > n_{eq}$, P increases. At $42 < n < 50$, we obtained $43 < P < 53$ (sample 3); these data are not presented in the figure.

The foregoing consideration shows that a rate of water desorption (at $n < n_{eq}$) in an air-free medium is limited by the surface process.

The following fact has engaged our attention; near the n values at which there are maxima in Fig. 3, the minima exist in Fig. 4, these minima being shifted toward the right; a steep maxima exists to the left of each minimum. Taking into consideration the data for the range $22 < n < 26$ (see above), it can be concluded that P mainly increases with n up to $P \approx 50$ for solutions characterized by $42 < n < 50$.

4. Discussion

The above results, as a whole, can be understood on the basis of the following picture of the H_2O sorption by PAA.

In PAA, just the AGs are the centres of water sorption. At most, AGs of the dry polymer are bounded by pairs forming quadrupoles,
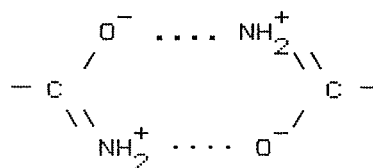
the rest of the AGs are dipoles.

When discussing the mechanism of dissolution in our interpretation, it is of little importance whether dried polymer molecules are globules or rods, whether they are tangled or thoroughly stacked, and whether they are monodisperse in a length chain or not. In any event, AGs are capable of pairing, but, because of the steric hindrances and limited mobility, some quantity of unpaired AGs exists. Our results show that vacuum heating of powdery PAA for 4 h at 373 K does not change its moisture capacity at 80–85% relative humidity. The moisture capacity of the starting material was ca. 100 mg of H_2O per 1 g of PAA, and the same material after vacuum heating was capable to sorb water vapour at ca. 80% relative humidity up to n=0.4, which is also equivalent to 100 mg of H_2O per gram of PAA.
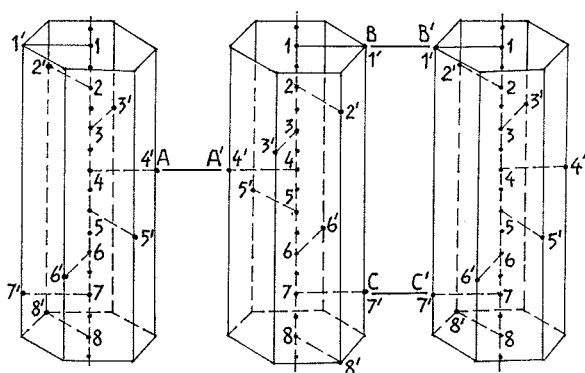
Fig. 5. Presumed structure of the clathrate-like compound I. Section along the main chains of PAA. Vertical rows of the numbers denote the tertiary C-atoms of the main chains of PAA molecules. Primed numbers denote the centres of the amido groups. Lines AA, BB and CC denote the AG–AG bonds.
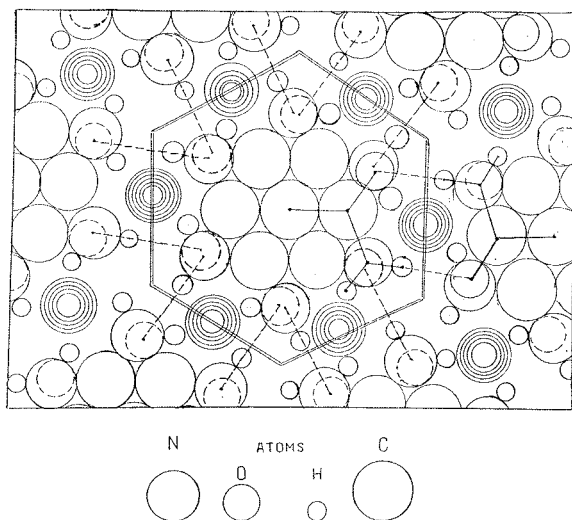

Fig. 6. Presumed structure of the clathrate-like compound I. Crosswise section through the main chains of PAA. Concentric circles denote the main structure 'windows' between polymer chains. Double line restricts an area of a cross section falling on one PAA molecule. Dashed lines show hydrogen-bonds ($O \cdots H-N$) binding together a central PAA molecule and the neighbouring ones. Solid lines give an example of two hydrogen bounded neighbouring AGs of different PAA molecules.

A peculiar sorption of H_2O proceeds across the whole volume of a sample in three sequential steps. At the first step, sorption of one water molecule near each unpaired AG occurs, since just such sorption gives the greatest gain in energy.

The second step is water sorption between AGs, into the inner space of each PAA molecule, up to $n=2$ (Figs. 5 and 6). At this step, the following transformations occur: linearization of the polymer molecules; breaking of the irregular intramolecular and also intermolecular AG–AG interactions; intramolecular structurization of each PAA molecule; and intermolecular structurization of the molecules 'filled' with water. Here, AGs draw up normally to the main carbon chain and organize a spiral around it, each AG being turned by $60°$ relative to the nearest neighbour; each PAA molecule linearizes and 'fills' with water up to $n=2$; the newly forming intermolecular structurization lies in the fact that each PAA molecule is encircled with a 'fence' of six molecules similar to the central one, forming regular AG–AG bonds between the nearest PAA molecules. It seems likely that this is just the type of structurization capable of giving a system of minimal energy. Needless to say, such a reorganization caused by water sorption does not proceed universally across the whole width of the sample. It may be suggested that the system tends to reorganize itself in such a manner. Straightening of the polymer globules, within concentrated solutions of polymers, with the reorientation of molecules and

formation of aggregates or bundles containing polymer molecules packed parallel, or almost parallel, to each other was assumed in Refs. [16,17]. These aggregates were considered as germs of a crystal phase.

At the third step, water sorption occurs outside each PAA molecule. At this step, germs of condensation are formed through the bonds of H_2O molecules by each AG–AG quadrupole and further growth of the ice-like clusters around these germs. The growth continues up to the equilibrium state corresponding to formation of the three-molecule-thick continuous water layer between the PAA molecules everywhere over the volume of the system.

On addition of water to the equilibrium PAA–H_2O system, H_2O molecules penetrate between the 'fences' of PAA molecules, moving them further apart with the formation of a solution. In the absence of agitation, this process is to be very slow because it proceeds without any heat effect as pure diffusion.

Sorption of a few water portions by dry polymer is accompanied by enhanced heat effects (Fig. 3). Such behaviour is caused by the fact that some of AGs are

single (unpaired), i.e. they are not joined into amide–amide (A–A) quadrupoles. Therefore, the heat of A–A destruction is not included in the heat of sorption being measured in these experiments. However, in a dry PAA the portion of unpaired AGs is small. A fraction of the H_2O molecules sorbed by unpaired AGs gradually falls off. Therefore, differential heats of sorption at $n<1$ abruptly decrease with n, the decrease arising from the exhaustion of the unpaired AG. In our experiments, the decrease of differential heats of sorption was observed up to $n=0.4$.

The observed rate of sorption is equal to the difference between the true rates of sorption and desorption. The rate of desorption and also the P value for the water molecules bonded together with the dipoles of the unpaired AGs is reduced (Fig. 4), since binding energy of these water molecules is higher than that of the water molecules sorbed at greater n values.

On further sorption, up to the merging of water clusters and formation of water continuity, water molecules are sorbed around each AG. In this process, the molar difference between the differential heat of sorption and the heat of water-vapour condensation at the liquid phase boundary is determined predominantly by the joint action of the following two factors:

(1) distinctions of the geometry of the outer water environment of any centrally sorbed water molecule from the tetrahedral environment of water molecules in liquid water; and
(2) the specific action of AGs on the water molecules being sorbed.

Just a manifestation of factor (1) is the cause of negativity of differential heats of sorption at certain n values. Factor (2) oppositely influences the heat of sorption by increasing it, since the dipole moment of AG ($M_{AG}=3.8$ D [18]) is stronger than that of a water molecule ($M_W=1.87$ D [19]). (Of even greater value, namely 4.9 D, is the dipole moment of a repeating unit of PAA, evaluated in [20], assuming the PAA contribution to the static permittivity to be completely due to a permanent electric dipole moment.)

Water tetrahedra grow concentrically around AGs. So long as the clusters are very small, an effect of the first factor on the differential heat of sorption is pronounced at such compositions of the system at which the next regular water tetrahedra around AGs only just begin to form ($n=5$, 9 and 13). When

formation of any regular tetrahedron is completed ($n=4$, 8, 12), some additional energy of stabilization is liberated; at $n=4$ this energy is so high that the differential heat of sorption exceeds the heat of vapour condensation.

The nature of phenomenon of energy stabilization is as follows. The centres of the positive and negative charges of water dipoles in a completed tetrahedron coincide with each other. Therefore, such states have no residual dipole moment. Disappearance of the dipole moments of water clusters at the intervals $3<n<4$, $7<n<8$, and $11<n<12$ results in decreasing the cluster energy and manifests itself in increasing the differential heat of water sorption (Fig. 3). Apparently, the water molecules placed in the inner space of the linearized PAA molecules reorient themselves at $n=4$, and tetrahedra water clusters originate.

When water molecules are sorbed by the cluster with completed tetrahedral structure of the outer water dipoles, the cluster dipole moment increases as the first three molecules are sorbed, the maximum increase taking place as the result of sorption of the first water molecule of the newly forming tetrahedron. A charging leads to an increase in the cluster energy. Therefore, the differential heat of sorption sharply decreases (Fig. 3, points 7, 9, and 11). At $n>16$, this effect comes to naught as a result of growth of the clusters, their confluence, and formation of water continuity.

After addition of superequilibrium water to the equilibrium PAA–H_2O system, PAA molecules would be forced to move progressively apart. Therefore, the effect of mutual linearization of the molecules dies away, and they are bent under heat fluctuations.

In this way, the integral pure heat of PAA dissolving (excluding heat of water vapour condensation at the surface of pure water) is taken up essentially entirely on increasing the n value up to n_{eq}. On dissolving PAA, a negativity of the heat effect is caused by the fact that the negative energy of the AG–AG bonds splitting cannot be entirely compensated for by the positive energy of the AG–H_2O bonds formation.

The negativity of the differential changes in Gibbs free sorption energy in all stages (up to $n=n_{eq}$) results from the following. In the stages of sorption, characterized by negativity of the pure differential heat effect, the process proceeds with the increase in pure differential entropy. This process is a result of the acts

of H_2O sorption leading to formation of the germ clusters with an uncompleted outer tetrahedron of water molecules, a sorbed H_2O molecule at every instant can equiprobably have more than one arrangement in the near-AG space. So long as the clusters are very small and the total quantity of the possible equienergy rearrangements of H_2O molecules in each of the clusters is not large, the noted effect introduces the essential additional contribution to the molar commutative entropy with respect to the entropy of the systems with $n=4$, 8 and 12 in which each cluster has in its outer sphere a completed tetrahedron of water molecules. A maximum additional contribution to the molar entropy of the PAA–H_2O system can be expected if a sorbed molecule is unique in the forming quartet of the outer tetrahedral water surrounding, i.e. on condition that the passages from $n=4$ to $n=5$, from $n=8$ to $n=9$, and from $n=12$ to $n=13$ take place as a result of sorption. In these cases, each sorbed water molecule can occupy any one of the four positions at each instant of time. Within the above-named n-intervals, the lowermost values of the differential heats of sorption are observed (Fig. 3). Apparently, the above-described entropy effect alone permits water sorption with the negative pure differential heat effects, compensating the latter by positive values of the changes in the pure differential entropy.

According to Ref. [20], the number of affected hydration H_2O molecules Z_h per AG of PAA at 298 K is equal to 5. This value was obtained by using the method of dielectric spectroscopy [21]. It correlates with the minima P observed by us at the n value between 4 and 5 (Fig. 4).

Finishing the discussion, let us sum our conclusions about phenomenology of the processes of water vapour sorption–desorption.

In air of 100% humidity, at room temperature, the equilibrium water content in the PAA–H_2O system corresponds to ca. 4.5 g H_2O per gram PAA ($n_{eq}=17$–18). Under such conditions, a rate of water sorption by dry PAA is at first limited by water diffusion from the atmosphere to the surface; after formation of a continuous mirror of the PAA–H_2O system (at $n>4$), the rate is limited by sorption at the surface.

At $n<n_{eq}$, in an air-free medium, the rate of water desorption is limited by the surface process. Under such conditions, a rate of establishment of an equilibrium is repeatedly increased on account of two

reasons: the former is chemical affinity between the H_2O molecules and AGs; the latter being superstandard entropy of the sorbed water.

At $n>n_{eq}$, under the atmosphere, desorption of the superequilibrium water is bridled by the air that blocks the water diffusion outwards from the surface.

In the air-free medium and under humidities of ca. 80%, a rate of water sorption by dry PAA is limited by sorption at the solution surface; the sorption arrests itself at $n=0.4$.

It remains to generalize our opinion on two questions:

> Why the volume process does not delay the establishment of the sorption-desorption equilibrium at $n<n_{eq}$? and
> What is the essence of the 'instability effects', observed at $n\gg n_{eq}$ [5] in this system?

In our opinion, the answers are interconnected.

Let us consider the first question. According to the above mechanism of sorption–desorption, PAA molecules at $1<n<n_{eq}$ are spaced some distance apart. In an air-free medium, the space between PAA molecules is devoid of any molecules up to $n=n_{eq}$. We observed the inception of minute vacuum bubbles in the bulk of PAA–water system in the process of H_2O desorption. The free space is being filled up with H_2O molecules as n increases. So, up to n_{eq}, water in the polymer matrix is half-gas, H_2O molecules having a high degree of freedom within the polymer phase. To put it differently, water molecules within the polymer phase have a superentropy essentially exceeding the entropy in liquid water. Therefore, in the air-free medium, the equilibrium in the PAA-H_2O system with $n<n_{eq}$ establishes quickly. In such a system, sorption–desorption is a surface-controlled process (as mentioned above), as if the system has no body.

It may appear that the high rate of equilibration observed in the desorption experiments is in conflict with a low rate of equilibration in the experiments on sorption from air of 100% humidity (Fig. 2). But that is not so. In the first case, the PAA–H_2O system is in an air-free medium, and the space between PAA molecules is free of air. In the second case, air molecules within the polymer phase sharply retard H_2O diffusion to the water clusters in the bulk of the PAA–H_2O system.

Now, we allow ourselves to make some assumption about the essence of the 'instability effects' in the PAA–H$_2$O system with $n \gg 18$. These effects come out, for example, in the prolonged, for some months, changes in solution viscosity [22], light scattering measurements yielding unchanged molecular weights [5].

Dissolving powdery PAA in liquid water proceeds in two steps.

The former is nothing but water sorption in the polymer up to the equilibrium state characterised by $n \equiv n_{eq} = 17$–18. This step shares a number of traits with the process proceeding under conditions of the experiment shown in Fig. 2. It proceeds spontaneously, since the free energy of the system decreases. But the rate of this step is retarded by the finest air bubbles localized within the polymer granules. These air bubbles delay water diffusion in the polymer phase.

The latter step is water diffusion within the phase of composition $nAG \cdot 18nH_2O$. This step proceeds with no gain in energy. Such a step is possible, since the energy of intermolecular AG–AG bond in the system of composition $nAG \cdot 18nH_2O$ is of the same order of magnitude as the thermal energy and since water evaporation from the superequilibrium system is severely limited by atmospheric air. This step is extremely slow. It seems likely that just this step of PAA dissolution is the chief cause of the instability effects reviewed in [5].

The possibility of solution stratification must not be ruled out. However, the density of hydrated PAA complexes of the composition $AG \cdot (4$–$5)H_2O$ forming after molecular dispersion of the $nAG \cdot 18nH_2O$ system is very close to the density of pure water, and the floatability of such complexes is very high. Therefore, if the solution stratification occurs, it is bound to be extremely slow.

The foregoing notion on the mechanism of the PAA–H$_2$O interaction allows us to explain qualitatively the nontrivial n-dependence of the rate of water desorption (Fig. 4). Most likely, the n-intervals, over which reduced values of the probability of desorption are observed, are associated with the n-intervals over which the disruption of the clathrate-like substance II (near n_{eq}), as well as of initial (near $n=4$) and second (near $n=8$) completed water tetrahedra occurs.

5. Conclusion

Evidently, the practically measurable value of the integral heat of dissolution of dry PAA is not constant, but depends on the rate of drying of PAA. The point is that the heat of dissolution is dependent on the degree of pairing of the AG-dipoles of dry PAA, the degree of bonding being poorly reproducible because to the poor mobility of the chains of the polymer being dried. As for the equilibrium degree of wetting (n_{eq}), it may not depend on the rate of drying.

The above-described view of a supposed structurization in the concentrated PAA–H$_2$O systems provides insight into the peculiarities of the calorimetric results; this view uses the data of Refs. [23–25] on the tendency of some organic amides to form liquid clathrate substances always having a hexahedral planar structure as well as on the fact that some clathrate compounds of different molecules with water contain 17 water guest-molecules per host-molecule (in our experiments $n_{eq} = 17$–18). Using these views and the tabulated data on the lengths of different chemical bonds (including the hydrogen-bonds), the density of aqueous solutions of PAA can be precalculated with a high degree of accuracy. For example, the density of a solution containing 2.0657 g PAA per 100 g of the solution was calculated as 1.00297 g/ml [26], the experimental value being equal to 1.00297 g/ml [27]. The obtained results allow us to propose non-contradictory thermodynamic explanation of the instability effects reviewed in Ref. [5].

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