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Comparison Study of the Acrylamide−Water and Polyacrylamide−Water Systems: Differential Heat Effects, Kinetics, and Mechanisms of Drying and Vapor-Phase Wetting

Victor E. Ostrovskii,* Bella V. Tsurkova, Elena A. Kadyshevich, and Boris V. Gostev

Karpov Institute of Physical Chemistry, ul. Vorontsovo Pole 10, Moscow 103064, Russia

Received: September 13, 2001

Differential data on the thermodynamics and kinetics of water-vapor sorption and desorption in the acrylamide−water system at room temperature and $0 < n < 74$ (n is the number of sorbed water molecules per amido group) are obtained. Water-vapor sorption from air of 100% humidity appears to be limitless. The magnitude of the differential molar enthalpy of sorption is about 25 kJ/mol for $n \ll 1$, passes through a maximum of 42 kJ/mol in the vicinity of $n = 1$ and a minimum of 24 kJ/mol in the vicinity of $n = 2$, and then approaches the level of the heat of water-vapor condensation on the pure water surface. The probability for a water molecule to desorb from the system into vacuum per unit time is observed to monotonically increase with n up to $n = 44$, with a small minimum for $n = 15−17$. In the system, a slight tendency for clathratization reveals itself in nonmonotonic dependences of $\Delta H(n)$ and $P(n)$, but no stable clathratization, as such, is identified. The results are compared with the corresponding data for the polyacrylamide−water system. The mechanisms of the sorption−desorption process are discussed.

Introduction

The mechanism of amide−water interaction has long been the subject of intensive study (e.g., refs 1−16). The interest in this subject is mainly driven by the facts that amides, along with amines, are of primary importance in living matter and that wetted monomer and polymer amides have many applications in chemical practice. In the past decade, different physical methods including NMR and Raman resonance spectroscopies[17−19] have been used for the clarification of questions related to the mechanisms and strength of hydrogen binding at amide−amide and amide−water interactions. However, many details of the mechanisms of amide−water interactions in highly concentrated solutions remain unknown.

In this work, we pursue the following principal goals: (1) acquisition of original differential data on the thermodynamics and kinetics of water-vapor sorption and desorption in the acrylamide (AA)−water system; (2) correlation between AA−water and polyacrylamide (PAA)−water systems and clarification of the carbon chain effect on the sorption−desorption process; and (3) clarification of the mechanisms of drying and water-vapor wetting at moderate degrees of wetting of the AA−water system.

Up to now, the differential molar enthalpies of drying and vapor wetting for amide−water systems have not been measured. It is known that the molar integral enthalpies for acrylamide (AA)[6] and polyacrylamide (PAA)[1,9] dissolving in liquid water at infinite dilution are positive and small in magnitude, like those for formamide and acetamide.[5,8] However, the question remained as to whether AA at room temperature can provide an infinitely diluted AA−water system through water-vapor sorption. In the event that such a possibility exists, the following questions arise: It is unknown whether the positive enthalpy term is associated with sorption by an amido group of the first, second, third, or tenth molecule of liquid water or,

perhaps, each of the water molecules successively entering into the amide−water system is sorbed with the same very small negative heat effect. This question is directly associated with two other questions that are no less important. Which water molecules being sorbed in succession near any one amido group are characterized by the "excess" partial molar entropy as compared with the liquid water entropy under the same external conditions? Also, is the excess entropy associated with a special mobility of water molecules, and if so, what is the mechanism of this mobility? Differential calorimetric measurements are necessary for clarifying these questions.

Numerous attempts, for example, refs 20−23, have been made to compute the strengths and lengths of hydrogen amide−amide and amide−water bonds with the molecular orbital method. Such techniques have been refined, and they provide realistic values only for isolated pairs of hydrogen-bonded molecules. However, at present, these computations are not capable of predicting bond strengths for condensed systems. The experimental data presented here can help guide such calculations.

The above-formulated questions and some other urgent issues related to the mechanisms of amide−water interaction were discussed by us earlier[14−16] as applied to the PAA−water system. Interactions within the PAA−water system are relevant to the pairing of adjacent DNA helixes through nitrogen bases in the DNA−water system. In these two systems, the binding of any two polymer molecules to one another is determined by the hydrogen $=O···HN=$ bonds modified by the water environment. As a consequence of experimental difficulties, the enthalpy of pairing of the nitrogen bases has not yet been measured, and in the opinion of the authors of ref 24, it is immeasurable. The enthalpies of guanine−cytosine and adenine−thymine pairing in a vacuum,[25] in chloroform,[26] and in dimethyl sulfoxide[27] are available. These data have been used for additive schemes[28,29] as applied to nonaqueous systems. For aqueous systems, only theoretical computations are available.[24,30,31] In ref 24, for guanine−cytosine and adenine−thymine pairing in water, free energies of roughly (−8) to (−12) kJ/mol per

* Author to whom correspondence should be addressed. E-mail: vostrov@cc.nifhi.ac.ru.

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hydrogen bond were computed using the AMBER potential energy function.

Our previous results[14−16] obtained for the PAA−water system led us to propose the existence of the quasi-equilibrium clathrate-like compound, $xAG \cdot (17-18)xH_2O$ [where x is the number of amido groups (AGs) in the system]. Many clathrate compounds with 17 "guest" water molecules per one "host" molecule are well-known. Hydrates $C_4H_4O \cdot 17H_2O$,[32] $(CH_2)_4O \cdot 17H_2O$,[33] $CH_3Cl \cdot 17H_2O$,[34] and $C_3H_6 \cdot 17H_2O$[35] and so-called mixed hydrates such as $C_3H_8 \cdot 2H_2S \cdot 17H_2O$,[36] $(CH_2)_4O \cdot 2H_2S \cdot 17H_2O$,[37] $C_3H_8 \cdot 2CH_4 \cdot 17H_2O$,[38] etc., are described in the literature. The clathrate hydrates of *n*-propylamine,[39] diethylamine,[40] and tertiary butylamine[41] are also known. All of these hydrates are characterized by the so-called structure II,[11] in which small and large cavities of well-known sizes are filled with "guest-1" and "guest-2" molecules, respectively.

Many tens of different hydrates are described in the literature (for example, refs 2 and 11). Therefore, there is reason to think that the capacity for hydrate formation is a basic property of water, rather than a property peculiar to a limited number of specific substrates. It is generally believed[2,11] that the principal conditions for hydrate formation are a molar water/substrate correspondence and also a geometric correspondence between the hydrate cavities and substrate molecules or atomic groups.

Experimental Procedures

Before describing the experimental procedures, we list the basic processes under study and the parameters measured: (1) stepwise, portion-by-portion water-vapor sorption from an air-free volume on preliminarily dried AA, with calorimetric determination of the differential molar enthalpies of sorption and fixation of the equilibrium water-vapor pressure as a function of the degree of wetting of AA; (2) stepwise, portion-by-portion vacuum desorption from the AA−water system, with calorimetric determination of the differential molar enthalpies and determination of the probabilities of desorption and of the equilibrium water-vapor pressure as functions of the degree of wetting of AA; and (3) water-vapor sorption from air of 100% humidity by preliminarily dried AA, with determination of the water quantity sorbed with time.

Additionally, ancillary experiments were performed to design the procedure of careful nondestructive drying of AA before the fundamental experiments.

The experimental procedures were little different from those used to study the PAA−water system[14−16] and other polymer−water systems.[42,43]

Calorimeter. We use a FOSKA differential heat-conducting double microcalorimeter[44,45] (the description of the FOSKA calorimeter from ref 44 is reviewed in ref 46, pp 55−56) with resistance thermometers as heat-flux sensors. Each thermokinetic curve characterizes the heat effect and kinetics of the thermal process; if the heat flux results from a single process with no side heat evolution, the thermokinetic curve characterizes the kinetics of this process. The area under the curve being measured from a pre-experiment zero line up to a post-experiment zero line (both are corresponding to the heat equilibrium within the calorimeter) is proportional to the heat effect. The proportionality coefficient is determined with the Joule heat evolution and is verified by measuring the well-known heat effects of chemical reactions. The sensitivity of the negative and positive flux measurements is 2.3×10^{-5} W. The time constant of the calorimeter is 170 s. The calibration procedures are detailed in refs 44, 45, and 47.
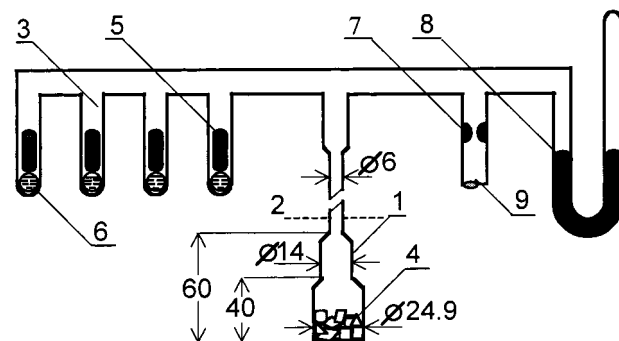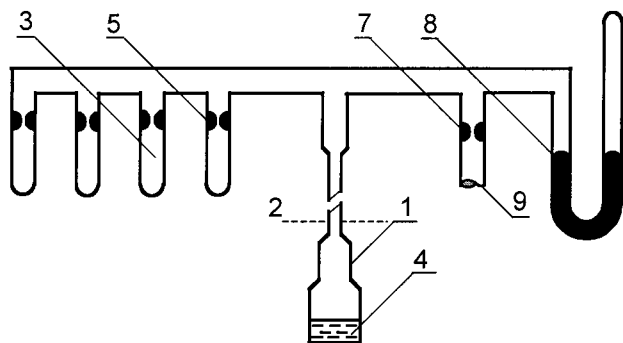

Figure 1. Apparatus for portion-by-portion water sorption: (1) calorimetric ampule, (2) top of the calorimeter, (3) test tube, (4) sample for wetting, (5) "breaker", (6) sealed water-containing glass sphere, (7) neck, (8) mercury manometer, and (9) tube to vacuum setup.

Glass Apparatus and Experimental Procedures. In Figure 1, a sketch of the glass apparatus for stepwise water sorption is presented. The apparatus (with a total volume of about 110 cm³) is portable; it is intended for experiments in air-free media. Before an experiment, the apparatus containing the sample (4), the "breakers", i.e., magnetic cylinders covered with glass (5), and the hermetically sealed glass spheres (6) with accurate weights (as a rule, 10−30 mg) of distilled water included are sealed at the section (9) to a vacuum setup with a trap that could be cooled by being immersed into a coolant. The ampule containing sample is cooled to 77 K by liquid nitrogen; after that, air is pumped from the apparatus, the apparatus is isolated from the pump, the trap is immersed into the liquid nitrogen, and the ampule is heated to 305 K and thermostated at 305 K for 3 h under 0.1 Pa inside a constant-temperature jacket. This preliminary treatment is performed outside the calorimeter. Then, the apparatus is sealed and cut off under vacuum across the neck (7), and the ampule (1) with the sample is lowered into the calorimeter so that, above the dashed line (2), the apparatus is outside the calorimeter.

The following procedure was applied to the sorption experiments in the calorimeter. After thermal equilibrium in the calorimeter has been established, we break one of the water-containing spheres by the magnetic cylinder via an outside magnet. The water begins to evaporate, and the sample inside the ampule lowered into the calorimeter begins to sorb the water vapor. In the course of the experiment, a thermokinetic curve is recorded, and a mercury manometer (8) gives the change in the water-vapor pressure over the sample. After the equilibrium water-vapor pressure has been achieved and the curve describing the thermal process in the sample has returned to the zero line (the deviation did not exceed 2.3×10^{-5} W), we break the next sphere filled with water, and so on [each apparatus has up to 14 tubes (3) supplied with glass spheres]. The rate of sorption decreases from one experiment to the next. The set of experiments is finished when, after a sphere has been broken, the water weight is not sorbed fully for 10−12 h.

In Figure 2, a sketch of the portable glass apparatus for stepwise desorption of water from the air-free AA−water system is provided. The apparatus (with a total volume of about 110 cm³) consists of an ampule with a sample, which can be lowered into the calorimeter, as well as tubes and a manometer, which remain outside the calorimeter during measurements. Accurately weighed portions of the substratum and water are placed into the ampule, the ampule is sealed to the apparatus, and the apparatus is sealed to the vacuum setup. Then, we pump out the sample and apparatus. For this purpose, we immerse the ampule with the sample into liquid nitrogen, pump it out to 0.1

Figure 2. Apparatus for portion-by-portion water desorption: (5) neck; for other notation, see Figure 1.

Pa, isolate it from the vacuum pump, heat it to room temperature, reimmerse it into liquid nitrogen, and repump it out to 0.1 Pa. Next, we seal off the apparatus under vacuum at point 7, reheat the ampule to room temperature, lower the ampule into the calorimeter down to the dashed line (Figure 2), and keep the sample at rest (i.e., we age it) at room temperature during a period indicated in Figures 4 and 6.

The following procedure was applied to the desorption experiments on studies of the differential enthalpies and probabilities of water desorption. Once thermal equilibrium between the sample and the calorimeter has been established, we immerse one of the tubes (3) (with a volume of about 1 cm^3) into liquid nitrogen. Desorption starts. As time passes (measured with a stop watch; as a rule, 60−300 s), we seal off the frozen tube containing a small mass (30−100 mg) of desorbed water. After the tube with the water collected is sealed off, the equilibrium pressure measured with the manometer (8) is gradually established just below (usually, by no more than 10−20%) the initial pressure. Thus, the heat measured corresponds to the enthalpy change at the transformation of the system from one equilibrium state to another. These two states differ from one another by the quantity of water collected in the tube. Once the thermal equilibrium temporally destroyed by desorption has been established, we immerse the next tube into liquid nitrogen and so on (each apparatus has up to 14 tubes). To determine the mass of water collected in each experiment, we weigh the sealed tube, cut it in two, and dry and weigh the dry cut tube. In each experiment a, in addition to the water mass desorbed, some water mass from the vapor phase over the sample is frozen (no more than 2.5% of the water mass desorbed). The heat effect of desorption of this additional water desorbed earlier is not measured in this experiment before the tube is sealed off. However, just after the tube with frozen water is sealed off, approximately the same water mass evaporates from the sample into the volume over it. During this water evaporation, registration of the heat effect of experiment a is continued up to the equilibrium. Thus, the heat effect of evaporation of the additional water mass is included rather accurately in the heat effect measured in experiment a.

For the experiments on water sorption from the atmosphere saturated by water vapor up to equilibrium, a weight glass with a dry AA sample is placed into a firmly closed desiccator containing a vessel filled with water. From time to time, we close the weight glass with a ground top, remove it from the desiccator, and weigh it. In the course of this experiment, room temperature varies. For example, at periods of 50−100, 650−800, 800−850, and 920−950 days, it was 290 ± 2, 290 ± 2, 292 ± 2, and 302 ± 1 K, respectively. Note that, in the experiments with the PAA−water system, at the period of

attainment of the quasi-equilibrium state, 330−390 days, the temperature was 290 ± 2 K.

Ancillary experiments are performed outside the calorimeter using a glass apparatus similar to that shown in Figure 2.

For each desorption experiment, we calculate a value P, which is proportional to the probability for each water molecule at the surface of the substrate−water system inside the calorimetric ampule to be desorbed into vacuum per unit time. We term below such values as "probabilities of desorption". For each water molecule, the stronger the water−substrate bond, the lower the probability of desorption. Therefore, the $P-n$ dependence indirectly characterizes the n dependence of the strength of the binding of water molecules in the sample. Hereafter, the n value is the number of water molecules sorbed per amido group of the substrate, $n = (H_2O)_{sorb}/(-C(O)NH_2)$. To introduce the concept of the probability of desorption, we start from a conclusion[16] on the limit of the rate of water desorption in a vacuum from the PAA−water system by evaporation from the surface rather than by volume diffusion. In those desorption experiments, three samples were used. The volumes of the samples were in the ratio of 1.28:1.00:2.54. However, for these samples, the rates of desorption measured at much the same n values differed by a factor of 1.05−1.15 only.[16] At room temperature, the rates of attainment of equilibrium in condensed bodies are usually much lower than the rates of attainment of gas−solid adsorption equilibria.[48] In the systems under consideration, they are high. Possibly, this fact results from the enhanced mobility of the water molecules within the defective hydrate structure. A high rate of attainment of heat equilibrium, after any desorption experiment is finished, corroborates our conclusion on the limitation of desorption by the surface process. The conditions of experiments with the AA−water system are no different from those with the PAA−water system.

Consider the surface of the fluid AA−water system in the experimental ampule to be a square grid, with each of L squares (L = constant) being occupied by one AA or H_2O molecule, and the surface molar H_2O-to-AA ratio to be equal to n. Then

$$L = l(H_2O) + l(H_2O)/n = l(H_2O)(n + 1)/n \qquad (1)$$

where $l(H_2O)$ and $l(H_2O)/n$ are the numbers of H_2O and AA molecules in the surface layer, respectively. The mean rate of isothermal stepwise water desorption from such a grid at a step characterized by a small change of the system from n to $(n - \Delta n)$ is

$$r = -\Delta l(H_2O)/\Delta \tau = Wl(H_2O) = WLn_m/(n_m + 1) = \\ Pn_m/(n_m + 1) \quad (2)$$

and

$$P = r(n_m + 1)/n_m \qquad (3)$$

where W is the probability of desorption of a water molecule per unit time and n_m is the n value corresponding to $l(H_2O) - \Delta l(H_2O)/2$. From the initial n value, the mass desorbed, and the duration of desorption, we compute P corresponding to each successive step of desorption. If a substrate−water system forms no specific molecular substances, it is reasonable to expect a monotonic $P-n$ dependence for a slightly wetted system and a constant P value for an infinitely dilute solution.

Experimental Errors. Experimental errors were considered by the example of the PAA−water system in ref 14 and, in less detail, in ref 16. Those considerations are basically true for the AA−water system as well. The metrology of the

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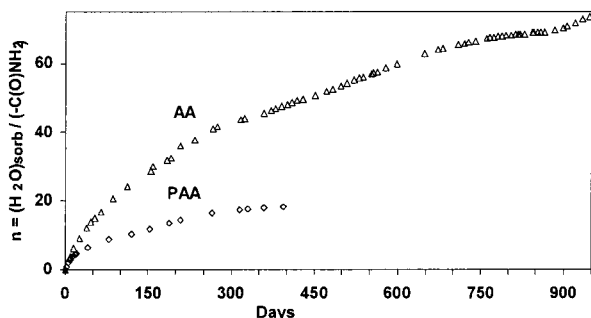
Figure 3. Kinetics of water-vapor sorption from the atmosphere of 100% humidity under a seasonal change in room temperature by samples 1 and 2 of PAA and AA ($\diamond$ and $\square$, respectively) and sample 1 of AA ($\triangle$).

calorimetric methods is developed principally in refs 44, 45, and 47. The metrology of measurements of the mass of sorption and desorption of water is developed principally in refs 42 and 43. All revealed sources of systematic inaccuracies exceeding 0.2% of masses and heats measured were taken into account in the computations. The random error in the mass of sorbed or desorbed water is 0.5%, and that in the molar heat effects is 0.7%. The mean absolute error in the differential molar heat effects is 0.30−0.35 kJ/mol. For the samples before desorption experiments, the absolute error in *the n* values (Δn) is within 0.05 ± 0.05. The error in the probability of desorption can achieve $\pm 10\%$.

Materials. AA and PAA were used as powders with a grain size of $<100\ \mu$m, or as solutions in distilled water. The polymer had a molecular mass of $(3-5) \times 10^6$ and contained one Na atom per 20−30 structural units. Note that our principal conclusions are independent of the granulation of the samples. It is clear that the experiments on desorption from the substrate− water systems are unaffected by the granulation. As the thermokinetic curves show, in each vacuum experiment on sorption, equilibrium throughout a particle is achieved. Thus, the granulation also has no effect on these experiments. The granulation has some effect on the rate of water sorption from air of 100% humidity; however, for $n > 2$, the substrates are fluids, and this effect disappears.

Results of Experiments

Ancillary experiments showed that, in a room with air of 80− 85% humidity, AA contains no more than 2−3 mg H_2O/g, i.e., the *n* value does not exceed 0.01. Under vacuum, water evaporates. Heating to 325 K leads to AA distillation and sublimation inside the apparatus. For comparison, we note that the PAA samples[14−16] were dried by vacuum heating at 358 K for 4 h (heating to 378 K does not enhance the total quantity of desorbed water).

Figure 3 provides data on water-vapor sorption by AA (sample 2) from air of 100% humidity in a desiccator at room temperature. After a lapse of more than 2.5 years, *n* achieved a value of 74, and it continues to increase. For comparison, results of two similar experiments for the PAA−H_2O system are given. In the latter system, equilibrium corresponds to $n = 17-18$.

Figure 4 provides differential enthalpy changes for water-vapor sorption and desorption in the AA−water system for $0 < n < 30$ within the air-free apparatus. For $n > 6.5$, the rate of sorption is too small for the heat emission to be measured accurately. For $n < 3.5$, the rate of desorption is too small for the heat of absorption to be measured accurately. For $n < 2-2.5$, water desorption terminates. For $n = 2.5$, the AA−water system comprises an extremely viscous fluid. If a sample is to be dry,
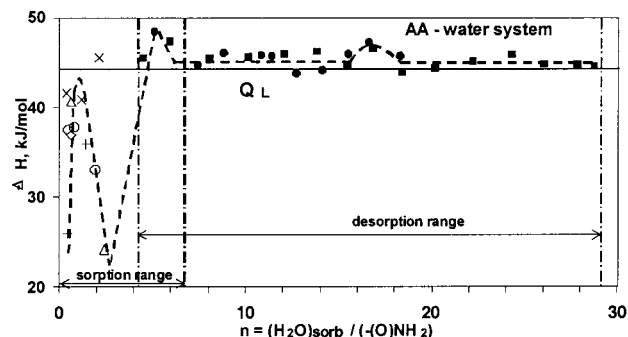
Figure 4. Differential molar enthalpies of water-vapor desorption from the AA−water system: sorption measurements with samples 6 (+), 7 ($\square$), 9 ($\triangle$), 11 ($\times$), 12 ($\bigcirc$), and 13 ($\diamond$) at 295, 294, 292, 290, 296, and 296 K, respectively, and desorption measurements with samples 1 ($\bullet$) and 4 ($\blacksquare$) at 291 and 290 K, respectively (samples 1 and 4 are aged after their preparation for 6 and 13 days, respectively). The experimental error is within the limits of the symbol sizes. The level Q_L corresponds to the molar enthalpy of water-vapor vaporization from the liquid pure water surface at 290 K.
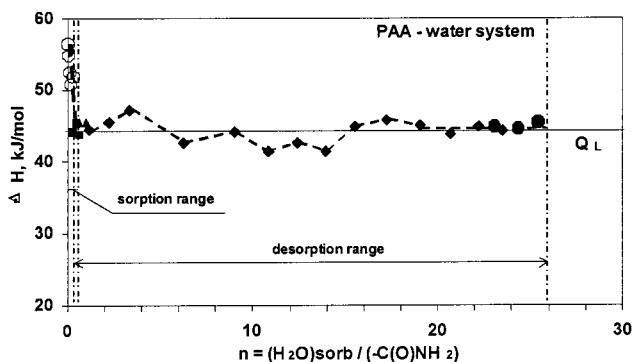
Figure 5. Differential molar enthalpies of water-vapor desorption from the PAA−water system: sorption measurements with sample 8 ($\bigcirc$) at 292 K and desorption measurements with samples 7 ($\blacksquare$), 10 ($\blacktriangle$), 11 ($\bullet$), and 9 ($\blacklozenge$) at 292, 297, 291, and 288 K, respectively (samples 7, 10, 11, and 9 are aged after their preparation for 14, 6, 16, and 9 days, respectively). The experimental error is within the limits of the symbol sizes. The level Q_L corresponds to the molar enthalpy of water-vapor vaporization from the liquid pure-water surface at 290 K.

it is necessary to heat it at 305 K in a vacuum for several hours. In Figure 5, data on differential enthalpy changes at sorption and desorption in the PAA−water system are provided for comparison. In this system, for $n > 0.7$, the rate of sorption is too small for the heat emission to be measured.

From Figures 4 and 5, it is obvious that the differential heats of sorption have no trend for $n \geq 18$. For the PAA−water and AA−water systems, for $n \geq 18$, the heat values are equal to 44.71 ± 0.49 and 44.84 ± 0.63 kJ/mol, respectively. Thus, the standard deviations are equal to 1.1 and 1.4% for the experiments with PAA and AA, respectively. Evidently, the absence of a trend for $n \geq 18$ means that, in this range, the systems studied can be approximately considered as the ideal solutions. For $n < 18$, the deviations of the differential heats of sorption from the mean values given above characterize the changes in the energy of the water−substrate interaction. It is seen that, at definite *n* values, these deviations significantly exceed the level of standard deviations.

The high quality of the calorimetric data permits us to believe that observed variations in the enthalpy [$\Delta H(n)$] adequately depict the actual characteristics of the systems under examination. On the basis of this conclusion, we relate the $\Delta H(n)$ and $P(n)$ variations to actual structural changes in the systems at some definite *n* values.
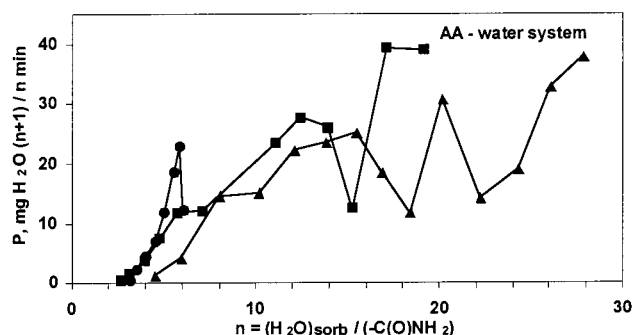
Figure 6. Differential probabilities of vacuum desorption from the AA−water system: measurements with samples 11 (●), 2 (■), and 4 (▲) at 290, 290, and 284 K, respectively (sample 11 is aged for 2 days after sorption experiments given in Figure 5, and samples 2 and also 4 are aged for 13 days after their preparation).

The sorption experiments were performed with initially dry AA, samples 6, 7, 9, and 11−13, and the desorption experiments were performed with AA dissolved in water, samples 1 and 4 (the mode of preparation of the samples is given above). Before the desorption experiments, samples 1 and 4 were aged for 6 and 13 days, respectively; sample 1 was additionally aged for 10 days after the fifth desorption experiment. The temperature of the calorimetric measurements is given in the figure captions and varies from 290 to 296 K. The level, Q_L, shown in the figure corresponds to the molar heat of water-vapor condensation at the surface of liquid water at 290 K.

Figure 6 contains data on probability (P) of water desorption as a function of the degree of wetting of the AA−water system. Corresponding data for the PAA−water system are available in ref 16.

When analyzing the data on the AA−water system, we should take into account two circumstances. First, it is clear a priori that ideal structuring in the semi-liquid systems under consideration is impossible. As seen in Figures 4 and 5, the differential molar enthalpies of water sorbed in the AA−water and PAA−water systems differ from the molar enthalpy of liquid water by no more than 4 kJ/mol everywhere over the range $n > 3$ on the background of the thermal energy $RT = 2.5$ kJ/mol. This means that the structuring, if the system tends to it, should be somewhat disrupted by molecular thermal movement and should depend critically on the temperature. Therefore, some temperature-dependent portion of extrastructural water could exist within the system. Thus, whereas the n value averaged over the body of the system can be determined rather precisely, the equilibrium local n value might vary somewhat from one point of the system to another. Therefore, the equilibrium in the system is easily disturbed and rather slowly established. In the course of a desorption experiment, such a disturbance should have a stronger effect on the probability of desorption than on the enthalpy of desorption. The heat effects in an experimental series at a constant temperature are measured from any one equilibrium state to another, including some small but noticeable (1−2%) postsorption heat effects. When measuring the probability of desorption, we assume that desorption in an experiment proceeds at a near-constant n value, i.e., that an equilibrium within the condensed phase is established during the period of desorption. Therefore, in isothermal experimental series, the precision of the $\Delta H - n$ dependence is significantly higher than the precision of the $P-n$ dependence. Second, it is necessary to bear in mind the fact that we do not measure the probability of desorption as precisely and accurately as we measure the mass and heat. Nevertheless, the former is of great importance for conclusions on the intermolecular interactions in the systems,

as P is exponentially dependent on variations in the energy of water affinity to the substrate. For two samples, the $P-n$ dependences have rather similar ordinates, but they are somewhat displaced from each other along the abscissa. This displacement is caused by an uncontrolled inequality of experimental conditions. Probably, in each of these experiments, equilibrium has not managed to be established, as the temperature is very low and the mass of water desorbed is rather great. Nevertheless, we note a rather clear minimum in the $P-n$ dependences for $n = 17 \pm 2$.

Figures 4−6 demonstrate a number of peculiarities requiring special consideration. Figures 4 and 5 show that the sorption−desorption processes proceeding in the PAA−water and AA−water systems have the following principal features. The differential enthalpies of sorption rise somewhat for $n = 4−6$ and 17 and fall to the value near Q_L for $n > 17−18$. For the AA−water system, the maxima near $n = 5$ and 17 are observed in two experiments performed at 290 and 291 K in the course of two different experimental series, the excesses in the differential molar enthalpy over the mean value exceeding the mean error by a factor of about 5. For the PAA−water system, the differences between the molar enthalpies observed for $n = 3.5$ and 6.5 and also for $n = 14$ and 17 exceed the mean error by a factor of about 10. This consideration gives grounds to the belief that the maxima observed are not artifacts. In Figure 6, moving from right to left along the abscissa, pronounced minima of the probability of desorption in the vicinity of $n = 15−17$ reveal themselves against the background of generally decreasing P.

In addition, Figures 4 and 5 show the following differences between the PAA−water and AA−water systems. Water-vapor sorption by PAA and AA from an air-free medium of 100% humidity almost ceases for $n = 1−2$ and $n = 6$, respectively. The endothermal contributions to the integral heat of substrate dissolving in liquid water are made predominantly within the ranges $5 < n < 15$ and $0 < n < 4$ in the PAA−water and AA−water systems, respectively. These conclusions follow from data on the enthalpies of water sorption and desorption. The nature of the phenomenon apart, we could say that the endothermal PAA and AA melting under conditions of water sorption finishes near $n = 15$ and $n = 4$, respectively. These are precisely the premelting and melting processes that determine the endothermal character of the integral process of dissolving. However, in the presence of water, melting is inseparable from the substrate−water interaction. Therefore, such a formal approach cannot clarify the nature of the phenomenon. Among other distinctions between the AA−water and PAA−water systems, we note that the initial enthalpy of water sorption by AA is well below and that by PAA is slightly above the Q_L level. Also, the differential enthalpy of water sorption by AA passes a maximum near $n = 1$ and a minimum near $n = 2$, whereas the enthalpy of sorption by PAA is near Q_L everywhere over the range $1 < n < 2$.

Some important results demonstrating the nontrivial effect of a gaseous atmosphere on the water sorption−desorption process proceeding in the systems under study are not reflected in the figures. These results are reviewed below. PAA sorbs water vapor from the air-free medium up to $n = 2$ only, whereas, at the same vapor pressure, as was indicated above, it sorbs water vapor from an air-containing medium up to $n = 17−18$. AA sorbs water vapor from the air-free medium up to $n = 6−7$, whereas, at the same vapor pressure, water-vapor sorption from the air-containing medium proceeds, apparently, without limit. In the air-free apparatus, at 100% humidity and 301−302 K,

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water evaporates spontaneously from the AA−water system and sublimates on the walls of the apparatus, whereas, under the same conditions in the air atmosphere, the AA−water system sorbs water vapor. One more effect well marked in the PAA−water system but barely perceptible in the AA−water system relates to this group of results. It is the "boiling" of the air-free PAA−water system immediately after the start of vacuum desorption of water. We intend to describe this phenomenon in more detail in another publication. Here, we note only that it reveals itself in the evolution of bubbles of vacuum from the system, lasts for some time after the termination of desorption of each water portion, and is accompanied by no heat effect. Evidently, these bubbles result from the aggregation of small empty cavities within the body of the fluid system that are caused by water desorption.

Discussion

We consider the data on wetting and drying of the AA−water system in the context of the principal goals listed in the Introduction and in the context of the mechanisms of wetting, dissolving, and drying of PAA. The mechanisms were assumed in ref 14, developed in ref 16, and annotated in ref 49. We do not consider in detail the grounds for assuming the mechanisms for the PAA−water system, but use data on this system for comparison only.

We believe that, in PAA, only AGs are centers of water sorption. In the dry polymer, most of AGs are duplicate and form quadrupoles

$$
\begin{array}{ccc}
& O(-)\cdots(+)NH_2 & \\
& /\!/ \qquad\qquad \backslash & \\
-C & & C- \qquad\qquad (4)\\
& \backslash \qquad\qquad /\!/ & \\
& NH_2(+)\cdots(-)O &
\end{array}
$$
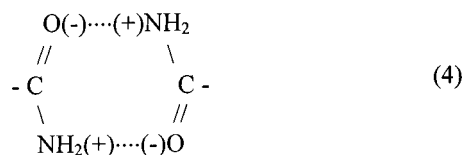
and the rest are dipoles. Hydrogen binding in crystalline AA is identified in ref 50. Water sorption by PAA proceeds over the entire volume of a sample in three steps. In step I, each unit AG possessing an uncompensated dipole moment sorbs a water molecule. In step II, water is sorbed between AGs, into the inner space of each PAA molecule, up to $n = 2$.[15] At this step, transformations within the system being wetted are as follows: straightening of the polymer molecules, breaking of the irregular intramolecular and intermolecular AG···AG interactions, intramolecular structuring of each PAA molecule, and intermolecular structuring of the PAA molecules "filled" with water.

In step III, the PAA molecules move somewhat apart so that each AG happens to be housed in a cavity formed by water molecules of hydrate structure II corresponding to the equilibrium composition $xAG \cdot 17xH_2O$.

Water sorption by an initially dry substance can be formally considered as a result of the summation of two processes, namely, substrate melting into an overcooled fluid and water sorption by this melt. In this connection, we note that dry AA at 357.5 K melts whereas dry PAA in the vicinity of 438 K becomes only soft, i.e., an increase in molecular mobility is achieved much more readily for AA than for PAA.

It is evident that, in both systems, only the polar AGs are centers of water sorption. Taken alone, the almost-nonpolar carbon chain has no significant action upon water sorption. It is clear that the difference in the substrate affinities to water is determined by peculiarities in the spatial arrangements of AGs within the polymer and monomer bodies. Unlike the monomer, mutual conformations of AGs in PAA are limited, as, in a

polymer molecule, a C atom of the chain is arranged between two adjacent AGs. This fact constrains multicoordination of AGs in the PAA structure. Therefore, the dipole moment of any one AG within the solid is neutralized by neighboring AGs to a greater extent in AA than in PAA. Most likely, each AG in the body of dry PAA is either paired with another AG or isolated, whereas each AG in the body of dry AA is coordinated with several neighboring AGs. Starting from this assumption, we explained in refs 14−16 the enhanced initial molar enthalpies of water sorption in PAA (Figure 5). On the basis of this assumption, it would be expected that the magnitude of the initial enthalpy of water sorption by AA is lower than the heat of water condensation on the surface of pure water. The results in Figure 4 show that the magnitude of the initial enthalpy change accompanying water-vapor sorption by AA is low; it is lower than Q_L by about 18 kJ/mol. For the process characterized by such a low heat effect to be thermodynamically possible, the decrease in the entropy (S) during this process must be smaller than that during water-vapor condensation at the water surface by at least 62.07 J/mol K. [This value is obtained from the condition that, at equilibrium with water vapor at 290 K, the change in Gibbs free energy for the AA−water system is equal to zero as for the H_2O (vapor)−H_2O (liquid) system, $\Delta(\Delta S) = (18\,000/290)$ J/mol K.] Nevertheless, the AA−water system for $0 < n < 1$ sorbs water vapor from liquid water spontaneously at 290 K and near-constant water pressure. This fact means that, in the first step of wetting, the AA−water system is characterized by a rather high molar entropy, as represented below.
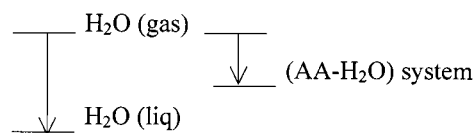
$$
\begin{array}{ccc}
\overline{\quad\quad}|\ H_2O\ (gas)\ \overline{\quad\quad} & & \\
& \Big\downarrow\ (AA\text{-}H_2O)\ system & \\
\Big\downarrow\ H_2O\ (liq) & &
\end{array}
$$

Figure 4 shows that the AA−water system being wetted passes through a stable state for $n = 1$ and through a metastable state for $n = 2$; for $n > 2$, the system fluidizes. We interpret these regularities as follows: The stable state with $n = 1$ is not fluid; most likely, it is a common monohydrate characterized by weakening of the $O(-)\cdots(+)NH_2$ bonds and by the formation of a water substructure in which each water molecule is arranged in the center of a tetrahedron consisting of the same molecules. Wetting up to such a state requires no principle rearrangement in the condensed phase; it proceeds in the AA−water and PAA−water systems in air-free media and also under the atmosphere. In air-free media, formation of the metastable state for $n = 2$ is characteristic for the AA−water system only. Evidently, for $n = 2$, an extremely "loose" water substructure is formed. In this structure, at every instant, each water molecule has equal chances of being localized in different points of the system. Possibly, we are dealing with the initial step of hydrate structure formation, when the system is swollen but structural vacancies are only partially filled with water molecules. It seems likely that there is no other way to explain the extremely high entropy of the AA−water system for $n = 2$.

There is a slight rise in the differential enthalpies of sorption near $n = 17$ and a fall to a near-Q_L value for $n > 17-18$. This leads us to suspect that, for some degree of wetting, the AA−water system, much like the PAA−water system, has a tendency for clathratization. In the case of the AA−water system, this tendency is less pronounced, as this system collapses easily near $n = 17$ upon subsequent wetting by saturated water vapor. With respect to water sorption from an atmosphere of 100% humidity, AA differs fundamentally from PAA (Figure 3). In the vicinity

of 290 K, the quasi-equilibrium quantity of water sorbed by PAA corresponds to the xAG·$(17-18)x$H$_2$O composition, whereas the monomer sorbs water apparently without limit. This result shows that, in the atmosphere of 100% humidity at about 290 K, AA forms no stable hydrate compound in contrast to PAA, which appears to be a hydrate-forming substrate.[14−16] The cause of the relative instability of the clathrate AA−water system near $n = 17$ lies in the fact that the hydrated AA molecules are much more mobile than the hydrated prolonged PAA structures. The xAG·$(17-18)x$H$_2$O structure in the AA−water system is unstable and dissociates rather easily into separate fragments. The process of dissociation is the cause of an additional entropy term in the entropy of water-vapor condensation at the surface of pure water. The nature of this term lies in the fact that the total quantity of different mutual arrangements of molecules in a system containing molecules of two types is larger than that in the equimolecular system of identical molecules. As the degree of wetting increases over $n = 17$, the degree of structuring decreases, and the system gradually approaches the model ideal solution. However, the AA−water system has a peculiarity. For this system, as for ideal solutions, the molar enthalpy of dilution is near-zero or at least well below the thermal energy, but the AA molecules are hydrated, and this fact influences the entropy of the system. Notice that, according to ref 12, in dilute aqueous solutions, amides are hydrated. PAA does not show any specific behavior.

Our results on the sorption−desorption of water confirm indirectly that we are dealing with the formation and destruction of hydrate structures. Such an effect is noncharacteristic for usual chemical compounds. However, it has long been known that inert gases (so-called auxiliary gases) have a pronounced stabilizing effect on hydrate formation.[51] For example, it is well-known that, near 273 K and 9.2×10^4 Pa, the air quantity sorbed by hydrate of chloroform is larger than that sorbed by H$_2$O by a factor of several tens.[52] This effect was interpreted[52] in the context of formal thermodynamic theory.[38,53]

Conclusion

In the absence of stirring and other disturbances, in certain cases, water molecules are able to form strictly determined cellular structures in the first stages of wetting of guest molecules or molecules containing guest valence-bound atomic groups of limited sizes. This ability reveals itself if the energy of such cellular structures is somewhat lower than the energy of the regular liquid state. At ambient temperature, this energy gain is near the molecular heat energy. Therefore, the hydrate structures can be destroyed under weak mechanical or thermal fluctuations, which results in the release of the guest particles and the formation of regular liquid systems. Evidently, similar clathrate-like hydrate structures can also exist in unperturbed fluid media.

We believe that the special features of the mechanisms of AA and PAA wetting and the peculiarities of the observed parameters of these processes are caused by difference in the mobility of the AGs and in the mutual symmetry of the neighboring AGs in these two systems when wetted only slightly. These differences between AA and PAA are conditioned by the occurrence of the carbon chain in the latter. The carbon chain decreases the degree of freedom for the AGs and also the strength and mean number of possible AG−AG (and also AG−H$_2$O) hydrogen bonds in PAA as compared to AA. The degree of freedom influences the kinetic parameters and the system states controlled by them. In particular, the state of source solid samples is determined by the conditions of drying

in the process of their production and by the kinetics of formation of the AG−AG hydrogen bonds in the solid body. In the processes of wetting and drying, the strength and mean number of possible hydrogen bonds influences the thermodynamic parameters and those kinetic parameters that are thermodynamically conditioned, such as the probability of water desorption. It is probable that the decreased degree of freedom for the AGs in the PAA molecules and the immobilization of the PAA−water system as a whole because of the occurrence of the polymer chains are the causes of an enhanced stability of the PAA hydrate in comparison with the AA hydrate.

The results obtained do not contradict the hypothesis[14−16] that the reversible self-organization of the half-liquid PAA−water system occurs up to critical water-to-substrate ratio $n = 17-18$. Apparently, the character of the self-organization depends on the experimental conditions and on the n value. In the AA−water system, there is some slight tendency for clathratization, but we did not identify rather stable clathratization as such. The tendency reveals itself in the nonmonotonic dependences of $\Delta H(n)$ and $P(n)$. We believe that the problem is worthy of additional examination, for example, by neutron scattering or X-rays. However, this is a rather specific problem with no simple solution. Indeed, it is not easy to create and conserve an equilibrium system of a prearranged degree of wetting within a cell for measurements, and most likely, such a study should be performed at slightly reduced temperature, when the value of RT is rather small.

References and Notes

(1) Silberberg, A.; Eliassaf, J.; Katchalsky, A. *J. Polym. Sci.* **1957**, *23*, 259.

(2) Hagan, M. M. *Clathrate Inclusion Compounds*; Reinhold, Chapman and Hall: New York, 1962.

(3) Assarsson, P.; Eirich, F. R. *J. Phys. Chem.* **1968**, *71*, 2710.

(4) Arnett, E. M.; McKelvey, D. R. In *Solute−Solvent Interactions*; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969.

(5) Stimson, E. R.; Schrier, E. E. *J. Chem. Eng. Data* **1974**, *19*, 354.

(6) Ostrovskii, V. E.; Artamonov, S. A.; Korneva, G. P.; Mamin, E. A. *Izv. Akad Nauk Kaz. SSR, Ser. Khim.* **1974**, 84.

(7) Soulier, J.-P.; Escoubes, M.; Douillard, A.; Chabert, B. *J. Chim. Phis.* **1976**, *73*, 423.

(8) Skold, R.; Suurkuusk, J.; Wadso I. *J. Chem. Thermodyn.* **1976**, *8*, 1075.

(9) Day, J. C.; Robb, I. D. *Polymer* **1981**, *22*, 1530.

(10) Kulicke, W.-M.; Knievske, R.; Klein, J. *Prog. Polym. Sci.* **1982**, *8*, 373.

(11) *Inclusion Compounds*; Atwood, J. L., Ed.; Academic Press: London, 1984; Vols. 1−3.

(12) Kaatze, U.; Gottman, O.; Podbielski, R.; Potel, R. *J. Mol. Liq.* **1988**, *37*, 127.

(13) Abramova, L. I.; Baiburdov, T. A.; Grigoryan, E. P.; Zil′berman, E. N.; Kerenkov, V. F.; Myagchenkov, V. A. *Poliakrilamid (Polyacrylamide)*; Khimiya: Moscow, 1992 (in Russian).

(14) Ostrovskii, V. E.; Tsurkova, B. V. *Zh. Fiz. Khim.* **1997**, *71*, 967.

(15) Ostrovskii, V. E.; Tsurkova, B. V. *J. Therm. Anal.* **1998**, *51*, 369.

(16) Ostrovskii, V. E.; Tsurkova, B. V. *Thermochim. Acta* **1998**, *316*, 111.

(17) Triggs, N. E.; Valentini, J. J. *J. Phys. Chem.* **1992**, *96*, 6922.

(18) Eberhardt, E. S.; Raines, R. T. *J. Am. Chem. Soc.* **1994**, *116*, 2149.

(19) Triggs, N. E.; Valentini, J. J. *Isr. J. Chem.* **1994**, *34*, 89.

(20) Mirkin, N. G.; Krimm, S. *J. Am. Chem. Soc.* **1991**, *113*, 9742.

(21) Duffy, E. M.; Severance, D. L.; Jorgensen, W. L. *Isr. J. Chem.* **1993**, *33*, 323.

(22) Guo, H.; Karplus, M. *J. Phys. Chem.* **1994**, *98*, 7104.

(23) Dixon, D. A.; Dobbs, K. D.; Valentini, J. J. *J. Phys. Chem.* **1994**, *98*, 13435.

(24) Stofer, E.; Chipot, C.; Lavery, R. *J. Am. Chem. Soc.* **1999**, *121*, 9503.

(25) Yanson, I. K.; Teplitskii, A. R.; Sukhodub, L. F. *Biopolymers* **1979**, *18*, 1149.

(26) Kuoguku, Y.; Lord, R. C.; Rich, A. *J. Am. Chem. Soc.* **1967**, *89*, 496.

(27) Newmark, R. A.; Cantor, C. R. *J. Am. Chem. Soc.* **1968**, *90*, 5010.

(28) Jorgensen, W.; Pranata, J. *J. Am. Chem. Soc.* **1990**, *112*, 2008.

Acrylamide−Water and Polyacrylamide−Water Systems

J. Phys. Chem. B, Vol. 105, No. 50, 2001 **12687**

(29) Schneider, H. *J. Chem. Soc. Rev.* **1994**, *22*, 227.

(30) Florian, J.; Sponer, J.; Warshel, A. *J. Phys. Chem. B* **1999**, *103*, 884.

(31) Abora, N.; Jayaram, B. *J. Phys. Chem. B* **1998**, *102*, 6139.

(32) Stackelberg, M. *Z. Electrochem.* **1958**, *62*, 130.

(33) Pinder, K. L. *Can. J. Chem. Eng.* **1965**, *43*, 271.

(34) Stackelberg, M.; Muller, H. *Z. Electrochem.* **1954**, *58*, 25.

(35) Clarke, E. C.; Ford, R. M.; Grew, D. N. *Can. J. Chem.* **1964**, *42*, 2027.

(36) Platteeuw, J. C.; van der Waalls, J. H. *Recueil Trav. Chim.* **1959**, *78*, 126.

(37) Pinder, K. L.; Keneth, Z. *Can. J. Chem. Eng.* **1964**, *42*, 132.

(38) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 41.

(39) Pouyet, B.; Mealier, P. C. *R. Acad. Sci.* **1964**, *259*, 2427.

(40) Jordan, T. H.; Mac, T. C. *J. Chem. Phys.* **1967**, *47*, 1222.

(41) McMullan, R. K.; Jordan, T. H.; Jeffrey, G. A. *J. Chem. Phys.* **1967**, *47*, 1218.

(42) Gostev, B. V.; Ostrovskii, V. E. *Zh. Fiz. Khim.* **1993**, *67*, 1127.

(43) Ostrovskii, V. E.; Gostev, B. V. *J. Therm. Anal.* **1996**, *46*, 397.

(44) Ostrovskii, V. E.; Dobrovol'skii, N. N.; Karpovich, I. R.; Frolov, F. Ya. *Zh. Fiz. Khim.* **1968**, *42*, 550.

(45) Ostrovskii, V. E.; Dyatlov, A. A.; Veselov, O. S. *Metrologiya* **1976**, *12*, 38.

(46) Gravelle, P. C. *Catal. Rev.-Sci. Eng.* **1977**, *16*(1), 37.

(47) Ostrovskii, V. E. In *Issledovanie kataliticheskikh protsessov (Metodicheskie voprosy kalorimetricheskikh isslodovanii)* [*Study of Catalytic Processes (Questions of Procedures for Calorimetric Studies)*]; NIITEKhIM: Moscow, 1977; p 3 (in Russian).

(48) Dushman, S. *Scientific Foundation of Vacuum Technique*; Wiley: New York, 1949.

(49) Ostrovskii, V. E.; Tsurkova, B. V. Presented at the 14th Experimental Thermodynamic Conference, Reading University, Reading, U.K., April 5−7, 1995. Ostrovskii, V. E. Presented at the 14th European Conference on Thermophysical Properties, Lyon, France, Sept. 16−19, 1996. Ostrovskii, V. E.; Tsurkova, B. V. Presented at the 15th Experimental Thermodynamic Conference; University of Surrey, Surrey, U.K., April 16−18, 1997. Ostrovskii, V. E.; Gostev, B. V.; Tsurkova, B. V. In *Energetics of Stable Molecules and Reactive Intermediates*; NATO ASI; Castelo Branco, Portugal, July 14−24, 1998; p 42. Ostrovskii, V. E.; Tsurkova, B. V.; Gostev, B. V.; Kadyshevich, E. A. Presented at the 16th IUPAC Conference on Chemical Thermodynamics, Halifax University: Nova Scotia, Canada, Aug. 6−11, 2000.

(50) Isakov, I. V. *Zh. Strukt. Khim.* **1966**, *7*, 898−899.

(51) Schroeder, W. *Die Geschichte der Gashydrate*; Enke: Stuttgart, Germany, 1926.

(52) Barrer, R. M.; Ruzicka, D. J. *Trans. Faraday Soc.* **1962**, *58*, 2239.

(53) Barrer, R. M.; Stuart, W. I. *Proc. R. Soc.* **1957**, *A243*, 172.