Physical Chemistry

Hydration of calixarene-containing polymers

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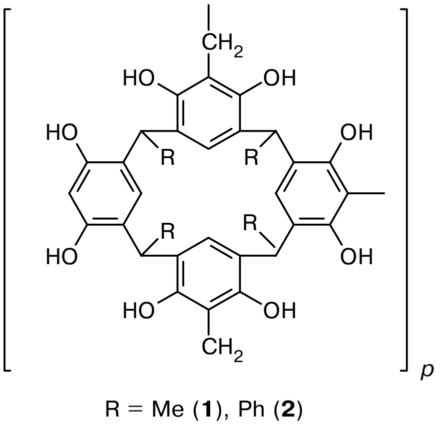
The hydration of cross-linked polymers containing tetramethylcalix[4]resorcinarene and tetraphenylcalix[4]resorcinarene was studied using the isopiestic, calorimetric, and MNDO/PM3 method. Adsorption of water vapor by calixarene-containing polymers leads to type II isotherms according to the Brunauer—Deming—Deming—Teller classification. In the framework of the Aranovich model of polymolecular adsorption, the monolayer capacity and pure heat of adsorption were calculated. The first monolayer is formed from 3-4 water molecules adsorbed due to hydrogen bonding with OH groups of calixarenes. The integral thermodynamic functions of hydration of the calixarene-containing polymers in water at 298 K were determined.

Key words: tetramethylcalix[4]resorcinarene, tetraphenylcalix[4]resorcinarene, polymer, hydration, isopiestic method, calorimetry, MNDO/PM3.

Hydrogen bonds play an important role in molecular recognition processes in biological systems. It has been established for water and sugar complexes with calixresorcinarenes in apolar organic solvents[1] that two hydrogen-bonded OH groups of the adjacent benzene cycles of tetraundekylcalixresorcinarene form an addition center for the OH group of the "guest" molecule.

In this work, we considered the hydration of polymers **1** and **2** with elementary units represented by fragments of tetramethylcalix[4]resorcinarene (**1**) and tetraphenylcalix[4]resorcinarene (**2**).



R = Me (**1**), Ph (**2**)

Experimental

Cross-linked polymers **1** and **2** were synthesized by the catalytic resol polycondensation of *cis*-2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene or *cis*-2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene with formaldehyde.[2,3] One kilogram of dry polymer **1** contained 1.34 moles of immobilized tetramethylcalix[4]resorcinarene, and the same weight of polymer **2** contained 0.92 moles of immobilized tetraphenylcalix[4]resorcinarene.

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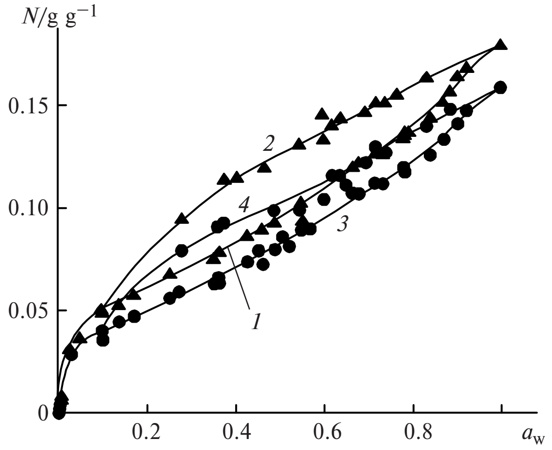

Fig. 1. Sorption isotherms of water vapor by calixarene-containing polymers **1** (*1*, *2*) and **2** (*3*, *4*) at 298.15 K: *1* and *3*, adsorption; *2* and *4*, desorption.

Sorption of water vapor by polymers **1** and **2** at 298.15 K was studied by the isopiestic method described previously.[4] Samples of sorbents under study were stored in an isolated vessel above a solution with a known constant activity of water. Solutions of H_2SO_4 with different concentrations were used as liquids with a desired vapor pressure of water. The experimentally obtained sorption isotherms of water vapor by polymers **1** and **2**, expressed as the amount of water adsorbed (N) against the activity of water (a_w) (Fig. 1) can be described according to the Brunauer—Deming—Deming—Teller (BDDT) classification[5] as type II isotherms. These isotherms correspond to polymolecular adsorption with a high heat. For both polymers, the hysteresis loop of the adsorption and desorption branches was observed. The hysteresis loop belongs, according to the classification presented in IUPAC recommendations, to type H3. Hysteresis loops of type H3 are characteristic of adsorbents having slit-like pores or consisting of planar-parallel particles.[5] Probably, polymers **1** and **2** contain elements of similar topology.

The experimental data on water vapor adsorption by polymers **1** and **2** were processed in the framework of the polymolecular adsorption theory using the Aranovich isotherm equation[6,7]

$$a_w/[(1 - a_w)^{1/2}N] = 1/CN_m + a_w/N_m. \qquad (1)$$

Here a_w is the activity of water; N_m is the capacity of the monolayer; $C = [\exp(-Q/RT) - 1]\rho_w/\rho_1$, where Q is the pure heat of adsorption, ρ_w is the density of water vapor, ρ_1 is the density of liquid, T is temperature, and R is the universal gas constant.

The integral free energy of hydration of the polymer (ΔG_{hydr}) was calculated from experimental data on polymer hydration with the activity of water defined as $a_w = P_w/P_0$ and using the equation[8]

$$\Delta G_{hydr} = \Delta G_1 + \Delta G_2 = -RT\int_0^{a_w} n d\ln a_w + nRT\ln a_w. \qquad (2)$$

The first term of Eq. (2) corresponds to a free energy change for adding one mole of the dry polymer to an infinitely great amount of water vapor with the partial pressure P_w, and the second term corresponds to a free energy change for transition of n moles of water from the pure liquid under the pressure P_0 to the vapor with the pressure P_w or to an infinitely large amount of the polymer, which is at equilibrium with water vapor at the partial pressure P_w. For the complete hydration of the polymer, the second term of Eq. (2) is equal to zero.

The thermal effect of hydration of polymers (ΔH_{hydr}) was measured with a DAK 1-1A differential microcalorimeter in the regime of autocompensation of thermal edf at 298 K. A KSPP-4 potentiometer served as a detecting device. A microcalorimeter was calibrated by the dissolution of chemically pure RbCl in water. The change in entropy (ΔS_{hydr}) for polymer swelling was calculated from the equation

$$\Delta G_{hydr} = \Delta H_{hydr} - T\Delta S_{hydr}.$$

The integral thermodynamic functions of hydration of calixarene-containing polymers in water at 298 K calculated per mole of the adsorbate are presented below.

Polymer	$-\Delta G_{hydr}$	$-\Delta H_{hydr}$	ΔS_{hydr}
	kJ mol^{-1}		/J mol^{-1} K^{-1}
1	17.1±0.7	5.3±0.5	39±6
2	17.0±0.8	4.4±0.4	42±5

Semiempirical quantum-chemical calculations were performed by the MNDO/PM3 method (MOPAC 3.5 program complex).

Results and Discussion

The quantum-chemical calculation of the structure and enthalpy of formation of *cis*-2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (**1**) and its complexes with water showed that hydration results in insignificant changes in interatomic distances **3**, and the calixarene remains in the boat-like conformation. The influence of the number of added water molecules (n) on the calculated enthalpy (ΔH_{hydr}) of the stepwise hydration of polymer **1**

$$\mathbf{1}\cdot(n - 1)H_2O + H_2O = \mathbf{1}\cdot nH_2O \qquad (3)$$

is shown in Fig. 2. It is seen that the enthalpies of addition of the first water molecules to compound **1** are

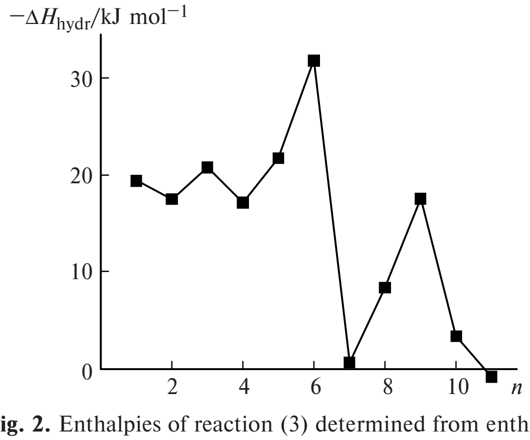

Fig. 2. Enthalpies of reaction (3) determined from enthalpies of formation of compounds at 298.15 K calculated by MNDO/PM3.

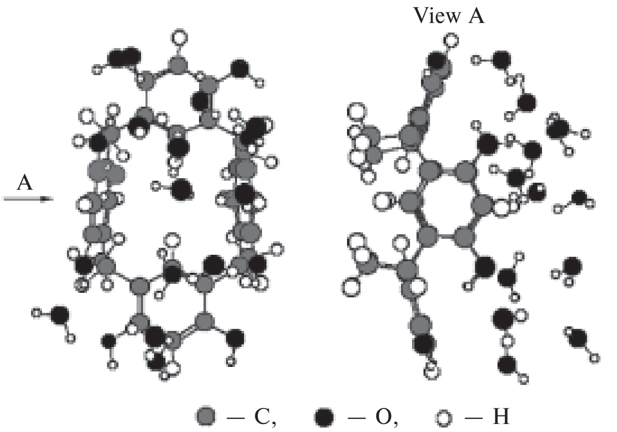

Fig. 3. Structure of complex $\mathbf{1} \cdot 12H_2O$.

virtually the same (-19 ± 1 kJ mol^{-1} H_2O). Probably, ΔH_{hydr} at $n < 5$ corresponds to the formation of hydrogen bonds between the H_2O molecules and OH groups of polymer **1**. An increase in the number of added H_2O molecules changes the character of the $\Delta H_{hydr}(n)$ function: most likely, each next H_2O molecule is added to $\mathbf{1} \cdot nH_2O$ by the formation of hydrogen bonds with water molecules.

It is seen from the structure of complex $\mathbf{1} \cdot 12H_2O$ optimized by the MNDO/PM3 method (Fig. 3) that layers composed of H_2O molecules lie above the surface formed by the OH groups of calixarene. The distance between the oxygen atoms of the water molecules of the first layer and OH groups of calixarene is 2.5—3.5 Å. If the $\mathbf{1} \cdot 12H_2O$ complex is considered from the viewpoint of the sorbent (calixarene)—sorbate (H_2O) interaction, its optimized structure corresponds to the Aranovich adsorption model.[6]

In fact, the experimental data on water adsorption by polymers **1** and **2** in the interval of water activities from 0.05 to 0.75 are well described by the Aranovich adsorption isotherm (Fig. 4). The same experimental points fit the BET equation for the a_w values ranging from 0.05 to 0.35. For all cases, the linear correlation coefficient is 0.99.

The experimentally obtained parameters of the adsorption isotherm (Eq. (1)) of water vapor by calixarene-containing polymers at 298.15 K processed by the least-squares method with a confidence probability of 0.95 are presented below.

Adsorbent	N_m /(g H_2O) g^{-1}	C	$-Q$ /kJ (mol H_2O)$^{-1}$	n_m* /mol mol^{-1}
1	0.073±0.004	19.0±8.4	33.7±1.0	3.0±0.2
2	0.066±0.003	12.4±2.1	32.6±0.4	4.0±0.2

* n_m is the number of adsorbed water molecules in the monolayer calculated per elementary unit of the polymer.

Comparison of the experimental and calculated data suggests that water adsorption by polymers **1** and **2** is of physical nature. The first adsorption layer is formed by the hydrogen bonding between three to four H_2O molecules and OH groups of calixarenes. Adsorbed molecules of the first layer serve as adsorption sites for molecules positioned in the second layer. The pure heats of adsorption (Q) are lower than the enthalpies of hydration (ΔH_{hydr}) of the polymers. It appears that the hydration of polymers includes, in addition to the energetically favorable interaction of water with adsorption sites, the extension of the polymeric matrix, which consumes energy. Polymer hydration is accompanied by an increase in entropy of the system.

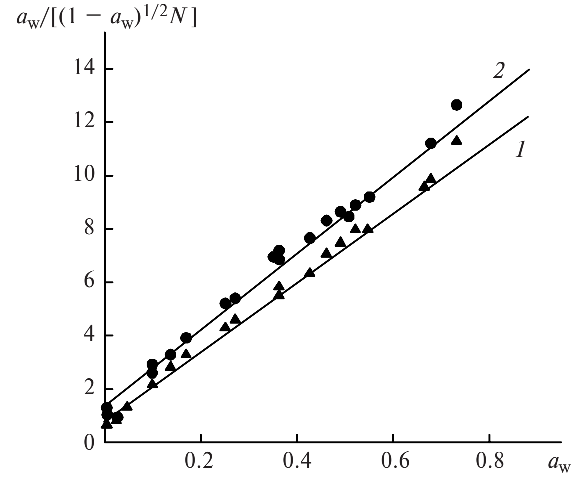

Fig. 4. Adsorption isotherms of water vapor by polymers **1** (*1*) and **2** (*2*) in coordinates of Eq. (1).

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