Adsorption of water isotopomers H_2O and D_2O on hypercross-linked polystyrene MN-272

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Adsorption of light and heavy water (H_2O and D_2O) on porous hypercross-linked polystyrene MN-272 was studied by gas chromatography. For the estimation of the properties of this polymer surface, *n*-alkanes (C6—C9), C_6H_6, and polar compounds ($CHCl_3$, $MeNO_2$, MeCN, Me_2CO, $EtCOOCH_3$, Et_2O) were used as test adsorbates. The contributions of energies of dispersion and specific (donor-acceptor) intermolecular interactions to the total energy of adsorption were determined on the basis of experimental data on the retention of the sorbates. The electron-donor and electron-acceptor characteristics of the hypercross-linked polystyrene MN-272 surface were estimated. Hypercross-linked polystyrene MN-272 was found to be a weakly specific adsorbent with predomination of electron-donating properties. The adsorption isotherms of H_2O and D_2O were measured on this polymer at 50, 60, and 70 °C. The dependences of the isosteric heats of adsorption on the amount adsorbed were determined. The contribution of the energy of specific interactions to the total energy of adsorption for all polar adsorbates (except for acetone, light and heavy water) does not exceed 20%. Adsorption of H_2O on hypercross-linked polystyrene MN-272 is slightly weaker than that of D_2O.

Key words: adsorption, gas chromatography, isosteric heats, isotopomers, light water, heavy water, hypercross-linked polystyrene.

Porous polymeric adsorbents differ in chemical nature, specific surface value, pore size, and pore size distribution, depending on the preparation conditions. This changes adsorption properties toward various classes of organic substances. The properties of polymeric sorbents of the new class, *viz.*, hypercross-linked polystyrenes, differ noticeably from those of usual polymers: porosity of the new type, the ability to swell in any liquid and gaseous media regardless of the affinity of the medium to polystyrene, and high adsorption activity.[1]

The purpose of the present work is to study adsorption of water isotopomers (H_2O and D_2O) on hypercross-linked polystyrene[2] MN-272 by gas chromatography and examine the dependence of adsorption of light and heavy water on the donating-accepting properties of the sorbent surface, which were estimated by the specific and nonspecific adsorption of a series of test organic compounds (*n*-alkanes and their nitrogen-, chlorine-, and oxygen-substituted derivatives, aromatic and heterocyclic hydrocarbons), whose molecules possess various electron-donating and electron-accepting properties.

Experimental

n-Alkanes (exhibiting only nonspecific (dispersion) interactions with the surface of any adsorbent) and benzene, THF, and polar derivatives of *n*-alkanes, which can enter specific (donor-acceptor) interactions with functional groups on the adsorbent surface, were used as adsorbates.[3] Selected characteristics of the adsorbates are listed in Table 1.

The porous hypercross-lined polystyrene polymer MN-272 (laboratory analog of the sorbent Purosep-200) was studied as an adsorbent.[4] The specific surface determined by the thermal desorption of nitrogen was 1142 $m^2 g^{-1}$, and the porous structure was mainly formed by micropores.

Table 1. Characteristics of test adsorbates*

Adsorbate	M	μ/D	α/Å^3	DN /kJ mol^{-1}	AN	DN/AN /kJ mol^{-1}
n-C_6H_{14}	86.18	0	11.9	0	0	0
n-C_7H_{16}	100.20	0	13.7	0	0	0
n-C_8H_{18}	114.23	0	15.6	0	0	0
$CHCl_3$	119.38	1.15	8.23	0	23	0
$MeNO_2$	61.04	3.54	7.2	11.3	20.5	0.6
MeCN	41.05	3.90	5.4	59.0	18.9	3.1
Me_2CO	58.08	2.80	6.6	71.1	12.5	5.7
MeCOOEt	88.11	1.80	9.0	71.5	9.3	7.7
Et_2O	74.12	1.70	9.5	80.3	3.9	20.6

* M is the molecular weight, μ is the dipole moment, α is the total polarizability of a molecule, AN and DN are the electron-acceptor and electron-donor energy characteristics of molecules.[3]

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 713—716, April, 2009.

The adsorption properties of MN-272 were studied by gas chromatography (GC) on a Cristallux-4000M chromatograph with the thermal-conduction detector. A glass tube with a length of 35 cm and an inner diameter of 2 mm was used as a chromatographic column. The weight of an adsorbent sample was 0.337 g. The carrier gas (helium) rate was maintained constant at ~25 mL $\min^{-1}$ when measuring the chromatographic retention parameters. Prior to experiment, the adsorbent was conditioned for 20 h in the chromatographic column in a helium flow at 200 °C. The liquid adsorbate probe 0.2—10 μL in volume was introduced into the injector of the chromatograph by a microsyringe.

The specific chromatographic retention volumes V_m were determined for all adsorbates in the temperature range 100—200 °C (for the sample 0.2 μL in volume).

Using the linear dependence of $\ln V_m$ on $1/T$ for the adsorbates, the differential mole changes in the internal adsorption energy $-\Delta U$ were calculated, which are equal to the differential mole heat of adsorption Q_v. The contributions of the energies of dispersion (Q_{disp}) and specific (Q_{spec}) interactions to the total adsorption energy (Q_v) were determined on the basis of the dependence of Q_v on the total polarizability of molecules.

For isotopomers of H_2O (99.996%) and D_2O (99.9%) in the temperature range 50—70 °C, the adsorption isotherms were plotted by a known procedure[5] taking into account the elution chromatograms (for samples 0.2—10 μL in volume). The isosteric heats of adsorption (Q_{st}) were calculated from the adsorption isotherms.

The porous structure parameters of MN-272 calculated on the basis of the isotherms of C_6H_6 and n-C_6H_{14} by the Dubinin—Radushkevich equation[6,7] are given below (a_0 is the limiting amount adsorbed, E_0 is the characteristic adsorption energy, L is the average width of slit-shaped micropores calculated by the Dubinin—Stoeckli equation: $L = 10.8/(E_0 - 11.4)$).

Adsorbate	a_0/mol g^{-1}	E_0/kJ mol^{-1}	L/nm
C_6H_6	2.1	16.0	2.3
n-C_6H_{14}	2.1	15.6	2.6

Results and Discussion

To estimate the role of contributions of dispersion and specific interactions to the adsorption on the porous hypercross-linked polystyrene polymer MN-272, we determined the dependences of $\ln V_m$ on $1/T$ for the isotopomer of H_2O and D_2O and a series of test adsorbates at small coverages of the sorbent surface for which the adsorbate—adsorbate interactions are not yet manifested noticeably.

The plots of $\ln V_m$ *vs* $1/T$ for all adsorbates in the temperature range studied (100—200 °C) are linear

$$\ln V_m = A + B/T, \qquad (1)$$

where $A = (\Delta S + R)/R$, $B = -\Delta U/R = Q_v/R$. The differential heats of adsorption Q_v for the H_2O and D_2O isotopomers and test adsorbates calculated from these dependences are listed in Table 2.

n-Alkanes interact with the surface of the hypercross-linked polystyrene sorbent MN-272 (as well as with all other adsorbents) only due to the dispersion forces (Q_{disp}), and their adsorption is determined by the geometric structure of the sorbents and total polarizability (α) of *n*-alkane molecules. The plot of Q_{disp} (kJ mol^{-1}) *vs* total polarizability of the *n*-alkane molecules is linear and is described by the following equation:

Table 2. Differential heats of adsorption (Q_v) and the contributions to the heats from dispersion (Q_{disp}) and specific (Q_{spec}) interactions (kJ mol^{-1}) for various adsorbates on the MN-272 polymer (α is the total polarizability of the adsorbate molecule)

Adsorbate	Q_v	α/Å^3	Q_{disp}	Q_{spec}	Q_{spec}/Q_v (%)
C_6H_{14}	54.8	11.9	54.8	0	0
C_7H_{16}	60.2	13.7	60.2	0	0
C_8H_{18}	67.4	15.6	67.4	0	0
C_6H_6	63.6	10.4	51.0	12.6	19.6
$CHCl_3$	55.2	8.2	44.8	10.5	18.9
$MeNO_2$	51.0	7.2	41.8	9.2	17.9
MeCN	46.9	5.4	36.8	10.0	21.5
Me_2CO	54.4	6.6	40.2	14.2	26.2
MeCOOEt	55.2	9.0	46.9	8.4	14.5
H_2O	44.8	1.5	25.5	19.2	42.5
D_2O	47.7	1.47	25.5	22.2	53.8
C_4H_8O	53.6	7.7	43.1	10.5	19.5
Et_2O	56.1	9.5	48.5	7.5	13.4

$$Q_{disp} = 3.3957\alpha + 14.1730 \ (R^2 = 1). \qquad (2)$$

Dispersion and specific interactions are manifested upon the adsorption of polar adsorbates. The contributions of the energy of specific interaction (Q_{spec}) were calculated by the formula $Q_{spec} = Q_v - Q_{disp}$, where Q_v is the total differential heat of adsorption of the test polar compound, and Q_{disp} is determined by Eq. (2) for hypothetical *n*-alkane, whose polarizability is equal to that of the test polar compound. The calculated values of total heats of adsorption and contributions to them of dispersion and specific interactions on MN-272 are given in Table 2.

The phenyl groups, whose π-electrons can specifically interact with functional groups of polar adsorbates, are mainly located on the surface of the hypercross-linked polystyrene polymers. However, on the polymer MN-272 the Q_{spec} value for all test adsorbates is slightly higher than that on nonpolar Chromosorb 103 (cross-linked polystyrene) and is considerably lower than those on Chromosorb 105 (polyaromatic ether)[8] and Chromosorb 104, whose surface contains nitrile groups.[9] Probably, surface of the polymer under study contains sites more active than π-electrons of phenyl groups (perhaps, these are oxygen-containing groups[10]).

The energy of specific interaction is determined by the donor-acceptor sorbate—sorbent interactions[11]

$$Q_{spec} = K_D\,\mathrm{AN} + K_A\,\mathrm{DN} \qquad (3)$$

or

$$Q_{spec}/\mathrm{AN} = K_D + K_A\,\mathrm{DN}/\mathrm{AN}, \qquad (4)$$

where AN and DN are the electron-acceptor and electron-donor numbers of the adsorbate molecules,[3] and K_D and K_A are the electron-donor and electron-acceptor characteristics of the adsorbent surface.

The dependence of the Q_{spec}/AN values on the DN/AN ratio is shown in Fig. 1. The K_D and K_A values determined from these dependences are 0.442 and 0.0731 kJ mol^{-1}, respectively.

Based on these data, we may conclude that the MN-272 surface contain both electron-accepting and electron-donating sites.

The contribution of the energy of specific interactions to the total adsorption energy does not exceed 20% for almost all polar adsorbates (except for acetone, light and heavy water). Thus, according to the data obtained, MN-272 is a weak specific adsorbent.[5]

Adsorption isotherms of H_2O and D_2O. The adsorption isotherms of H_2O and D_2O on MN-272 at 50, 60, and 70 °C are shown in Fig. 2, *a*. They have a pronounced sweep (Fig. 2, *b*) in the region of low amounts adsorbed (a = 0—0.3 mmol g^{-1}). This indicates that the polymer surface contains active hydrophilic sites, which are centers for the primary adsorption of light and heavy water. Molecules adsorbed on these sites become, in turn, secondary[12] centers for the adsorption of H_2O and D_2O molecules.

At low coverages (below a = 0.3 mmol g^{-1}) at all temperatures, the isotherms of H_2O lie higher than the isotherms of D_2O. For higher coverages (at a > 0.3 mmol g^{-1}) the sorption of D_2O becomes stronger than that for H_2O, especially at 70 °C. Inversion in the course of the isotherms is related, probably, to small differences in the adsorbate—adsorbent and adsorbate—adsorbate interactions and to the properties of molecules of the H_2O and D_2O adsorbates. At low relative pressures, when the adsorbate—adsorbent interactions are most important, the adsorption of H_2O and D_2O occur due to the energy of dispersion interactions, which is proportional to the polarizability of the molecules. Since the polarizability of an H_2O molecule is somewhat higher than that for a D_2O molecule (by 1.47 Å^3),[13] H_2O molecules are strongly adsorbed in the area of low coverages. Adsorbate—adsorbate interactions (hydrogen bonds) begin to play the determining role in adsorption with an increase in the surface coverage. The interactions are stronger in heavy water, because the intermolecular bond OH—O is somewhat weaker than the OD—O bond (the O—D hydrogen bond is shorter than in the case of O—H).[14] Accordingly, adsorption isotherms of D_2O lie above the isotherms of H_2O at all temperatures studied. The difference in the amounts adsorbed of D_2O and H_2O increases with temperature and the amount adsorbed (see Fig. 2, *a*).

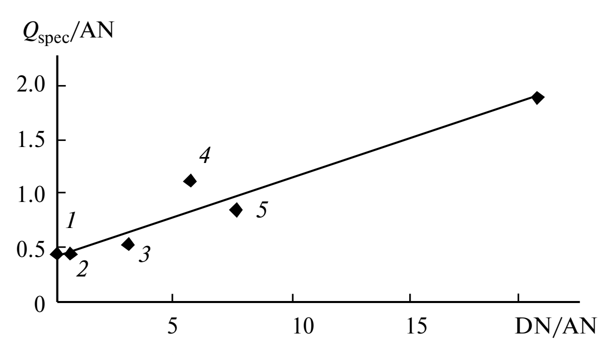

Fig. 1. The Q_{spec}/AN values used for the determination of the electron-donor (K_D) and electron-acceptor (K_A) characteristics of the polystyrene MN-272 surface as a function of DN/AN: $CHCl_3$ (*1*), $MeNO_2$ (*2*), MeCN (*3*), Me_2CO (*4*), EtCOOMe (*5*), and Et_2O (*6*); $y = 0.0731x + 0.442$ ($R^2 = 0.9335$).

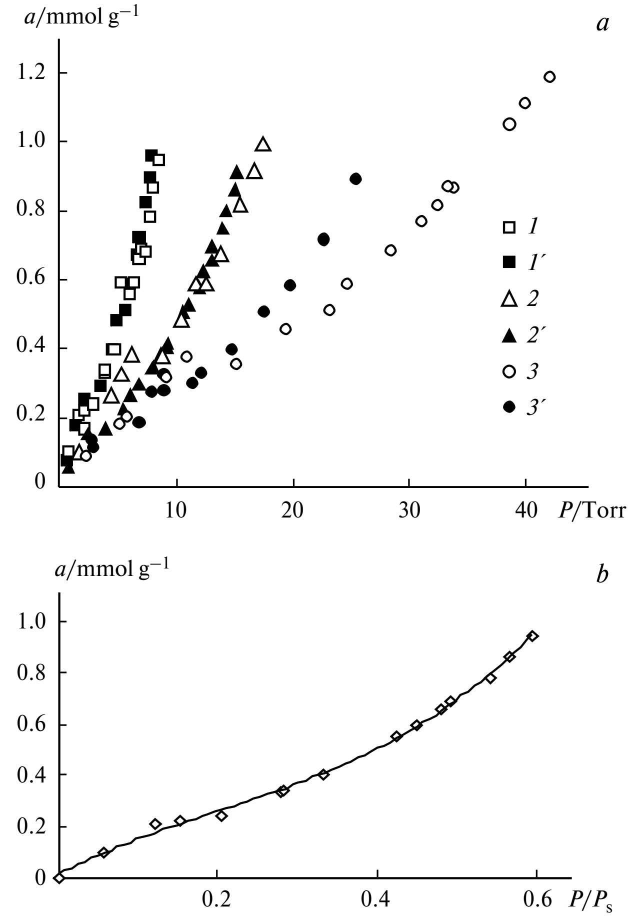

Fig. 2. Adsorption isotherms on polystyrene MN-272 at 50 (*1*, *1′*), 60 (*2*, *2′*), and 70 °C (*3*, *3′*): H_2O (*1—3*) and D_2O (*1′—3′*) (*a*); the amount of adsorbed water against the surface coverage at 50 °C (*b*).

Heats of adsorption. The isosteric heats of adsorption at different coverages of the polymer surface were determined from the adsorption isotherms by the equation

$$d\ln p/dT = Q_{st}/(RT^2). \quad (5)$$

The dependences of Q_{st} on the amount adsorbed a for the H_2O and D_2O isotopomers are shown in Fig. 3. The high values of the heat of adsorption of H_2O and especially D_2O at low amounts adsorbed (a = 0.05 mmol g^{-1})

also indicate that the surface of this polymer contain a low amount of strong adsorption sites. After their coverage, already at $a = 0.1$ mmol g^{-1}, the heat of adsorption of the H_2O vapor is slightly higher (by ~8.4 kJ mol^{-1}) than the heat of condensation of the H_2O vapor at 60 °C ($L_{H_2O} = 43.0$ kJ mol^{-1}) and then increases slightly with the amount adsorbed. On the nonpolar nonporous adsorbent with the homogeneous surface (graphitized thermal carbon black) Q_{st} is considerably lower than the heat of condensation in the entire region of surface coverages.[15] This also indicates a weakly polar character of the surface of the MN-272 polymer. The heats of adsorption of D_2O in the region of surface coverages below amounts adsorbed of 0.3 mmol g^{-1} slightly exceed the heats of condensation of D_2O vapors at 60 °C ($L_{D_2O} = 43.2$ kJ mol^{-1}). At higher coverages ($a > 0.3$ mmol g^{-1}) the Q_{st} value for D_2O is lower than the heats obtained for H_2O. Probably, this is due to the diffusion of D_2O molecules to the polymer bulk at 70 °C (with the absorption of D_2O molecules in the polymer bulk) and to a possible adsorption deformation and a change in the adsorption field in micropores upon the adsorption interaction.[16] It is known that both adsorption of substances on the surface and sorbate dissolution in the whole volume of polymer particles take place in the case of porous polymers.[17] The both retention mechanisms can appear simultaneously, especially at higher temperatures and amounts adsorbed. In this case, the heat of sorption is the sum of the heat of adsorption and heat of absorption. The heat of absorption is always smaller than the heat of adsorption, because absorbed molecules execute the work against the cohesion forces of the polymer chains.

Thus, it follows from the obtained data that hypercross-linked polystyrene MN-272 is a weakly polar adsorbent. Its surface contains both electron-donating and electron-accepting sites. Polar organic substances are adsorbed on MN-272 due to both dispersion interactions and weak donor-acceptor interactions. The contribution of the energy of specific interactions to the total adsorption energy does not exceed 20% for almost all studied polar adsorbates (except for H_2O, D_2O, and Me_2O). The adsorption properties of D_2O and H_2O on the polymeric sorbent MN-272 somewhat differ; under the conditions considered, D_2O is adsorbed somewhat more strongly than H_2O.

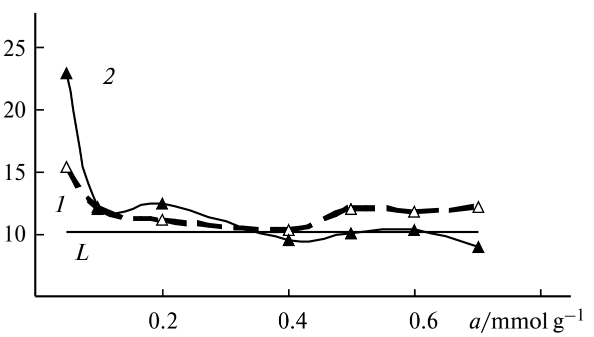

Fig. 3. Curves of the isosteric heat of adsorption (Q_{st}) of H_2O (*1*) and D_2O (*2*) against the amount adsorbed (calculated taking into account the isotherms at 50—70 °C); *L* is the heat of H_2O condensation at 60 °C.

This work was financially supported by the European Union (6th Framework Program, contract 5032, 2005) and the Russian Foundation for Basic Research (Project Nos 06-03-33131, 06-03-32995, and 09-04-00867).

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Received October 10, 2007;
in revised form March 4, 2008