Description of adsorption of haloalkanes and haloarenes on graphitized thermal carbon black by means of the model of an ideal two-dimensional gas

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The standard entropies theoretically calculated for 40 haloalkanes and haloarenes adsorbed on graphitized thermal carbon black were compared with those determined from the adsorption-chromatographic data. It was found that a molecular model of an ideal two-dimensional gas is a sufficiently good approximation in all the cases. For a number of systems, agreement can be improved by taking into account the vibrations of the center of the molecular mass relative to the surface.

Key words: halocarbons, graphitized carbon black, gas-adsorption chromatography, model of an ideal two-dimensional gas.

It is known that the gas-chromatographic technique can often be used successfully for the determination of thermodynamic characteristics of adsorption in the Henry region where the linear equation of the isotherm is valid:[1]

$$\Gamma = K_{1,c} \cdot C. \tag{1}$$

Here Γ is the adsorption, mmol m^{-2}; C is the concentration of an adsorbate gas, mmol cm^{-3}, and $K_{1,c}$ is Henry's constant, cm^3 m^{-2} (hereinafter the subscript 1 indicates that the value concerns the Henry region).[2] The main starting assumption for the use of chromatographic data in calculation of thermodynamic values is the following: the thermodynamic constant $K_{1,c}$ is set equal to the corrected retention volume $V'_{A,1}$, which is measured experimentally.[1] The following approximate relation describing the temperature dependence of $V'_{A,1}$ is commonly used for processing the experimental chromatographic data:

$$\begin{aligned}\ln V'_{A,1} \equiv \ln K_{1,c} = \bar{q}_{\mathrm{dif},1}/(RT) + (\Delta\bar{S}^{s°}{}_{1,c}/R + 1) \approx \\ \approx B/T + A.\end{aligned} \tag{2}$$

Here $\bar{q}_{\mathrm{dif},1}$ is the differential heat of adsorption,[2] $\Delta\bar{S}^{s°}_{1,c} = \bar{S}^{s°}_{1,c} - \tilde{S}^{\circ}_{g,c}$, where $\bar{S}^{s°}_{1,c}$ is the standard (Γ = 1) differential entropy of an adsorbed substance, $\tilde{S}^{\circ}_{g,c}$ is the standard (C = 1) molar entropy of an adsorbate in the gas phase; R is the gas constant. Under this approximation, coefficients A and B and consequently $q_{\mathrm{dif},1}$ and $\Delta\bar{S}^{s°}_{1,c}$ are assumed to be independent of temperature in the temperature range under study. The following relation between the differential ($\bar{S}^{s°}_1$) and integral (average molar) ($\tilde{S}_1{}^{s°}$) entropies[3] was also used:

$$\bar{S}_1{}^{s°} = \tilde{S}_1{}^{s°} - R. \tag{3}$$

Previously[4,5] some attempts to represent the physical state of an adsorbed substance as a two-dimensional ideal or real gas have been made. Such a model of a two-dimensional gas was suggested as an alternative to the model of localized adsorption (*e.g.*, for the Langmuir model). One can expect that the adsorbed substance is similar to a two-dimensional gas that moves parallel to the adsorbing surface when this surface is very uniform and contains no centers of possible localization of the adsorbate molecules. Graphitized thermal carbon black (GTCB) is believed to be an ideal adsorbent of this type.[2] It is expedient to apply the model of an ideal two-dimensional gas precisely to the systems containing GTCB as the adsorbent. The correspondence of this model to the real system can be examined, for example, using the $\Delta\bar{S}^{s°}_{1,c}$ value, which, on the one hand, is determined experimentally (see relation (2), $\Delta\bar{S}^{s°}_{1,c}$(exp.)) and, on the other hand, is calculated by the formula obtained by the methods of molecular statistics[6] taking into account relation (3):

$$\begin{aligned}-\Delta\bar{S}^{s°}{}_{1,c}(\mathrm{theor.}) = \tilde{S}^{(3)}{}_{\mathrm{trans}} - \tilde{S}^{(2)}{}_{\mathrm{trans}} + R = \\ = R\ln(MT)^{1/2} + 56.95 + R,\end{aligned} \tag{4}$$

where M is the molecular mass of an adsorbate, $\tilde{S}^{(3)}{}_{\mathrm{trans}}$ and $\tilde{S}^{(2)}{}_{\mathrm{trans}}$ are the translational contributions to the integral entropy of three-dimensional and two-dimensional gases, respectively (see, *e.g.*, Ref. 7). By definition, an ideal two-dimensional gas differs from the usual three-dimensional gas by a loss of one translational degree of freedom.

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Previously we carried out the calculation by formula (4) for more than 200 systems, where organic compounds of different classes were used as adsorbates and GTCB was used as the adsorbent (see, *e.g.*, Refs. 6, 8—10). The calculated $\Delta\bar{S}^{s^\circ}_{1,c}$(theor.) values were compared with the $\Delta\bar{S}^{s^\circ}_{1,c}$(exp.) values obtained from the experimental chromatographic data. With allowance for the accuracy of chromatographic measurements, the experimental data do not contradict the model of an ideal two-dimensional gas in the majority of cases. The difference between $\Delta\bar{S}^{s^\circ}_{1,c}$(exp.) and $\Delta\bar{S}^{s^\circ}_{1,c}$(theor.) exceeded 15% only in rare instances. These differences are likely due to either the partial localization of adsorbed molecules or to the contribution of vibrations of the centers of their masses relative to the surface of the adsorbent (in these two cases, the deviations of $\Delta\bar{S}^{s^\circ}_{1,c}$(exp.) from $\Delta\bar{S}^{s^\circ}_{1,c}$(theor.) have a different sign) or due to other reasons, *e.g.*, an increase in systematic experimental errors when the temperature of the runs increases.

In this work, $\Delta\bar{S}^{s^\circ}_{1,c}$(exp.) were compared with $\Delta\bar{S}^{s^\circ}_{1,c}$(theor.) for 40 adsorption systems in which various halocarbons were used as the adsorbates and GTCB was the adsorbent.

Experimental[11]

Gas-chromatographic measurements were carried out on a Pye chromatograph with a β-ionization detector. The velocity of the carrier-gas (argon) was 20—40 mL min^{-1}. Measurements were performed at temperatures from 294 to 488 K at 4—5° intervals. The adsorbent was Sterling MT-3100 (D4) graphitized thermal carbon black (the specific surface area was 7.65 m^2 g^{-1}). The carbon black was preformed as small balls without a binder. A fraction of 0.3—0.4 mm balls was used for packing the 120 cm×2.5 mm glass column. The weighed portion of carbon black was 4.42 g with a total surface area of 34 m^2.

As the molecular masses of adsorbates increased, the temperature range for the compounds under study was shifted to the higher temperatures. The recorded temperature of the column somewhat deviated from the true value due to imperfection of the chromatograph (the absence of preheating of the carrier gas), and this fact could change the values of the retention volumes, producing a systematic error.

Results and Discussion

Table 1 presents the $\Delta\bar{S}^{s^\circ}_{1,c}$(exp.) values obtained experimentally and the $\Delta\bar{S}^{s^\circ}_{1,c}$(theor.) values calculated by formula (4). Temperature T is the average temperature of the range studied, $q_{\mathrm{st},1} = q_{\mathrm{dif},1} + RT$ is the isosteric heat,[3] and ΔT is the temperature range of the experimental runs.

The following conclusions can be drawn from the data presented in Table 1. a. In all the cases with one exception, $|\Delta\bar{S}^{s^\circ}_{1,c}(\mathrm{theor.})| \geq |\Delta\bar{S}^{s^\circ}_{1,c}(\mathrm{exp.})|$. b. Deviations of $\Delta\bar{S}^{s^\circ}_{1,c}$(exp.) from $\Delta\bar{S}^{s^\circ}_{1,c}$(theor.), *i.e.*, $\Delta(\Delta\bar{S}^{s^\circ}_{1,c}) = |\Delta\bar{S}^{s^\circ}_{1,c}(\mathrm{theor.}) - \Delta\bar{S}^{s^\circ}_{1,c}(\mathrm{exp.})|$ exceed 10 J mol^{-1} K^{-1} in 14 cases and 15 J mol^{-1} K^{-1} only in three cases. c. It can be seen when comparing the analogous Cl-, Br-, and I-substituted alkanes that the $\Delta(\Delta\bar{S}^{s^\circ}_{1,c})$ values increase on going from Cl to I. d. The highest values of $\Delta(\Delta\bar{S}^{s^\circ}_{1,c})$ are observed for CH_2Br_2, CH_2I_2, and Me_3CCl.

When one assumes that all the above deviations are statistically *significant*, *i.e.*, are not caused by experimental errors, and are due to the contribution to the entropy of the low-frequency vibrations of the center of molecular mass relative to the surface ($\bar{S}^{(2)}_{\mathrm{vibr}}$), then $\bar{S}^{(2)}_{\mathrm{trans}}$ can be replaced by $\bar{S}^{(2)}_{\mathrm{trans}} + \bar{S}^{(2)}_{\mathrm{vibr}}$ in formula (4). This means the introduction of an additional vibrational contribution to the statistical sum of the adsorbed molecule. Then $\Delta(\Delta\bar{S}^{s^\circ}_{1,c}) = \bar{S}^{(2)}_{\mathrm{vibr}}$.

It was suggested in the simple model of an ideal two-dimensional gas resulting in formula (4) that all "inner" contributions to the statistical sum of a molecule, *i.e.*, vibrational and rotational, and especially the electron contributions do not change during transition from a gas to an adsorbed state. However, one should take into account that the translational degree of freedom, which corresponds to movement perpendicular to the surface of the adsorbent, in fact does not vanish (this results in formula (4)) but transforms into the low-frequency vibration whose frequency is approximately equal[12] to several tens of cm^{-1}. This vibrational contibution should be taken into account in the calculation of the two-dimensional statistical sum. This can be done (see also Ref. 2, p. 238) by multiplication of the translational contribution $Q_N{}^{(2)}{}_{\mathrm{trans}}$ for N molecules of a two-dimensional gas by the vibrational contribution $Q_{N,\mathrm{vibr}}$, where

$$Q_{N,\mathrm{vibr}} = q^N{}_{1,\mathrm{vibr}} = \{1 - \exp[-h\nu/(kT)]\}^{-N}. \quad (5)$$

Here ν is the vibration frequency, h is the Planck constant, and k is the Boltzmann constant. It is convenient to change from ν to the wave number $\tilde{\nu}$:

$$\tilde{\nu} = \nu/c \text{ (in cm}^{-1}\text{)},$$

where c is the velocity of light. When the values of constants are substituted, then

$$h\nu/(kT) = x = 1.4388\cdot\tilde{\nu}/T. \quad (6)$$

It is easy to obtain from expression (5) the formula for the vibrational contribution to the entropy[7] that is referred to 1 mole ($N = N_A$, where N_A is the Avogadro number):

$$\tilde{S}_{N_A,\mathrm{vibr}} = R\{x/[\exp(x) - 1] - \ln[1 - \exp(-x)]\} \approx$$
$$\approx R(1 - \ln x) = R[1 - \ln(1.4388\cdot\tilde{\nu}/T)]. \quad (7)$$

The right side contains the expression for $\tilde{S}_{N_A,\mathrm{vibr}}$ under the so-called quasi-classical approximation ($kT \gg h\nu$). In our case of low frequencies and relatively high temperatures, this approximation gives a nearly exact result. The value $\tilde{S}_{N_A,\mathrm{vibr}} = \bar{S}_{N_A,\mathrm{vibr}}$ is inferred as a correction (with minus in accordance with the sign of $\bar{S}^{(2)}_{\mathrm{trans}}$) to the right side of formula (4). It is not difficult to find with the aid of formula (7) that if $\Delta(\Delta\bar{S}^{s^\circ}_{1,c})$ (17.5 J mol^{-1} K^{-1}, see Table 1, CH_2I_2) is set equal to

$\bar{S}_{N_A,\text{vibr}}$, then we get the following value for the wave number at $T = 350$ K: $\nu \approx 80$ cm^{-1}. This is generally in line with evaluations available in the literature, especially for the adsorbed molecules weakly bound to the surface.[12] It should be noted that the frequency is not only due to the depth of the potential minimum on the curve describing the energy of the adsorbate—adsorbent interaction but also to its "sharpness", *i.e.*, the curvature in the vicinity of the minimum, although both characteristics are interrelated. The latter characteristic depends also on both the configuration and the volume of a molecule. According to Table 1, it is noteworthy that the highest values of $\Delta(\Delta\bar{S}^{s\circ}_{1,c})$ are typical of molecules with a small number of atoms but containing Br and I atoms with relatively large atomic radii.

When the correction $\Delta(\Delta\bar{S}^{s\circ}_{1,c})$ decreases, the vibration frequency calculated by formula (7) increases rapidly; hence, the quasi-classical approximation cannot be used for its estimation. At $\Delta(\Delta\bar{S}^{s\circ}_{1,c}) = 10$ J mol^{-1} K^{-1}, $\bar{\nu} \approx 300$—350 cm^{-1}. The problem of vibrations of an adsorbed molecule relative to the surface has long attracted the attention of researchers, but all attempts to determine the frequency experimentally by spectral methods failed, as did the use of the methods of quantum chemistry. Nevertheless, our estimation of $\bar{\nu}$ seems to be reasonable and does not contradict the approximate calculations on the basis of the curvature near the minimum, although, as was already said, the deviation $\Delta(\Delta\bar{S}^{s\circ}_{1,c})$ can be due to other reasons. This problem requires additional study.

Table 1. Comparison of $\Delta\bar{S}^{s\circ}_{1,c}$(theor.) and $\Delta\bar{S}^{s\circ}_{1,c}$(exp.) for a series of organic halogen compounds adsorbed on GTC

Adsorbate	Mol. mass	$\hat{T}$/K	ΔT/K	$-\Delta\bar{S}^{s\circ}_{1,c}$(theor.) /J mol^{-1} K^{-1}	$V'_{A,1}{}^{373\text{ K}}$ /mL m^{-2}	$q_{st,1}$ /kJ mol^{-1}	$-\Delta\bar{S}^{s\circ}_{1,c}$(exp.) /J mol^{-1} K^{-1}
EtBr	109	334	295—373	108.9	0.18	28	97.6*
EtI	156	349	325—373	110.6	0.49	31	97.3*
Pr^{n}Cl	78.5	334	295—373	107.7	0.34	31	100.3*
Pr^{n}Br	123	349	325—373	109.6	0.67	33	100.1*
Pr^{n}I	170	349	325—373	110.9	1.77	36	100.0*
Bu^{n}Cl	92.5	349	325—373	108.4	1.33	37	105.1*
Bu^{n}Br	137	349	325—373	110.2	2.60	38.5	103.5*
Bu^{n}I	184	377	325—428	111.7	6.50	41.5	104.0*
n-$C_5H_{11}Br$	151	405	373—438	111.1	10.5	44	107.1*
n-$C_6H_{13}Cl$	120.5	413	373—453	110.2	20.0	48	112.0*
n-$C_6H_{13}Br$	165	418	373—463	111.6	41.0	50	111.4*
n-$C_6H_{13}I$	212	431	373—488	112.8	94.0	53	112.6*
Pr^{i}Br	123	334	295—373	109.4	0.51	31.0	97.0
Pr^{i}I	170	356	325—388	111.0	1.27	33.9	97.2
2-BuCl	92.5	362	332—393	108.6	1.07	34.1	99.1
2-BuBr	137	370	332—408	110.2	2.00	36.3	99.8
2-$C_5H_{11}Br$	151	398	358—438	111.0	6.7	42.3	105.8
2-$C_6H_{13}Br$	165	405	373—438	111.4	24.0	48.1	110.8
Me_3CCl	162.5	334	294—373	110.6	0.49	29.9	94.4
Me_2CHCH_2Br	137	363	328—398	110.1	1.86	36.2	100.2
Me_2CHCH_2I	184	390	358—423	111.7	4.7	39.2	100.5
$Me_2CHCH_2CH_2Cl$	106.5	393	353—433	109.3	3.6	39.5	103.5
$Me_2CHCH_2CH_2Br$	151	393	353—433	110.9	6.3	41.4	103.9
$CHCl_3$	118.5	334	295—373	109.2	0.41	31.8	100.9
CCl_4	154	334	295—373	109.3	0.82	33.1	98.7
CH_2Br_2	174	334	294—373	110.9	0.55	30	93.7
$CHBr_3$	253	386	343—428	112.9	3.0	40	106.4
CH_2I_2	268	401	343—458	113.3	3.8	36.8	95.8
$C_2H_4Cl_2$ (1,1)	99	352	325—378	108.8	0.61	30.6	94.4
$C_2H_3Cl_3$ (1,1,2)	132.5	370	332—408	110.2	1.91	36.5	101.0
$C_2H_2Cl_4$ (1,1,1,2)	168	390	343—438	111.4	3.5	37.8	99.2
$C_2H_2Cl_4$ (1,1,2,2)	168	413	373—453	111.6	6.2	41.8	105.2
C_2HCl_5	202.5	403	368—438	112.3	12.3	44.0	105.3
C_2Cl_6	237	413	373—453	113.0	14.1	46.1	109.8
$C_2H_4Cl_2$ (1,2)	99	334	294—373	108.5	0.57	32	98.7*
$C_2H_4Br_2$ (1,2)	188	356	325—388	111.4	2.4	37	100.1*
PhF	96	393	358—428	109.1	0.86**	41.4	107.4
PhCl	112.5	433	403—463	110.1	3.4**	47.2	109.2
PhBr	157	433	403—463	111.5	5.9**	48.6	107.0
PhI	204	448	413—483	112.7	13.1**	51.0	107.4

* The data are taken from Ref. 11. ** The $V'_{A,1}$ values are presented at 423 K.

Unlike our previous studies, noticeable and one-way (although small) deviations from the simple model of an ideal two-dimensional gas are typical for the systems considered in this work. A correction with account of the vibrations of the adsorbate molecule relative to the surface of an adsorbent was shown to be possible. The estimation of the frequencies of these vibrations results in reasonable values. However, in this case, the *a priori* calculation (*i.e.*, in the absence of the corresponding experimental data) of the $\Delta\bar{S}^{s\circ}_{1,c}$ values cannot be carried out with sufficient accuracy.

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