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MOLECULAR-STATISTICAL CALCULATION OF THE THERMODYNAMIC CHARACTERISTICS FOR SEPARATION OF DEUTERATED MOLECULES BY ADSORPTION

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SUMMARY

Calculations have been made of the ratio of the retention volumes, the differences in the isosteric heats and differential entropies of adsorption for the pairs of the isotopic-substituted molecules $\text{CH}_4\text{-CD}_4$, $\text{C}_2\text{H}_6\text{-C}_2\text{D}_6$, $\text{C}_3\text{H}_4\text{-C}_3\text{D}_4$, $\text{C}_6\text{H}_6\text{-C}_6\text{D}_6$ and $\text{C}_6\text{H}_{12}\text{-C}_6\text{D}_{12}$ on graphitised carbon blacks. The differences in the potential functions of the interaction between the isotopic molecules and the adsorbent surface and the differences in the quantum effects for the vibrations of the isotopic molecules mass centres normal to the surface have been taken into account. The results of the calculations are compared with experimental data found in the literature. The differences in the quantum effects for the vibrations of the mass centres of the hydrocarbon isotopic molecules normal to the surface are small and only appreciable for the lightest molecules. The isotopic effect on adsorption of the hydrocarbon molecules on graphitised carbon blacks is mainly caused by the difference in the potential functions of the interactions of isotopic molecules with the surface. The zero point energy effect can also contribute to the isotopic effect for hydrocarbon molecules.

INTRODUCTION

The adsorption properties of isotopic molecules slightly differ¹⁻²⁵. Depending on the mass and the structure of the molecule, the nature of the surface and the temperature, deuterated molecules may be adsorbed both more strongly^{1-10,10-22} or more weakly^{16-18,21,23-25} than the hydrogenated form.

The isotope effect on the adsorption is apparently caused by three following factors: (1) the differences in the potential functions Φ of the interaction between the isotopic molecules and the adsorbent surface (the quantum mechanical effect); (2) the differences of the quantum effects in adsorption for the external (translational and rotational) degrees of freedom of isotopic molecules, due to the difference of their masses and moments of inertia; and (3) the different change of intramolecular vibrational energy of the isotopic molecules on adsorption, due to the difference of the

masses of the vibrating atoms (the zero-point energy effect). As a first approximation these effects can be regarded as independent.

The potential functions Φ for the deuterated and the hydrogenated forms of hydrocarbon molecules must always apparently differ somewhat. In the case of adsorption on a non-polar surface this effect causes a decrease in the adsorption of the deuterated molecules, and in the case of heavier molecules, this is apparently the main effect^{26,27}.

The translational and rotational quantum effects always increase the adsorption of deuterated molecules by comparison with the adsorption of the hydrogenated form. These effects, however, decrease rapidly when the mass and moment of inertia of the molecule and the temperature increase, but they are considerable for the lightest molecules at low temperatures. In the case of hydrogen isotopes the quantum effects for the external degrees of freedom are the main ones^{10,28,31}.

Depending on the sign of the change of the force constants of intramolecular vibrations in the adsorption, the zero-point energy effect can cause either an increase or a decrease in the adsorption of deuterated molecules. With an increase of the temperature, this effect decreases considerably more slowly than the quantum effects for the external degrees of freedom. The contribution of this effect increases with an increase in the number of substituted atoms. Therefore the zero-point energy effect may be significant for hydrocarbon molecules with a great number of the substituted atoms^{23,32,33}.

Of these three effects only the quantum effects for the external degrees of freedom have been investigated to any extent^{10,28-31}. The quantum mechanical and the zero-point energy effects have been investigated much less extensively^{23,26,27,32}.

We have calculated the potential functions Φ of the interaction between a number of the isotopic molecules ($\text{CH}_4\text{-CD}_4$; $\text{C}_2\text{H}_6\text{-C}_2\text{D}_6$; $\text{C}_2\text{H}_4\text{-C}_2\text{D}_4$; $\text{C}_6\text{H}_6\text{-C}_6\text{D}_6$; $\text{C}_6\text{H}_{12}\text{-C}_6\text{D}_{12}$) and the basal face of graphite on the basis of the physico-chemical properties of the isotopic molecules and the graphite lattice. The ratio of the retention volumes, differences of the isosteric heats and differential entropies of adsorption for these systems of isotopic molecules at zero coverages were calculated from the calculated potential functions.

In a previous paper²⁷, the groups of atoms were assumed to be the force centres of the molecules. In this paper the atoms are assumed to be the force centres of the molecules. This approximation allows for an apparently better representation of the spatial structure of the molecules under consideration.

STATISTICAL EXPRESSIONS

The ratio of the retention volumes V_s for a pair of isotopic molecules at zero coverage and at a fixed temperature T and surface area A is given by the following general expression³⁴:

$$V_s^{\text{H}}/V_s^{\text{D}} = (Q_1^{\text{H}}/Q_1^{0\text{H}} - 1)/(Q_1^{\text{D}}/Q_1^{0\text{D}} - 1), \quad (1)$$

where Q_1 and Q_1^0 are the partition functions for one molecule in a volume V in the presence and in the absence of the adsorbent, respectively. The upper indices H and D refer to the hydrogenated and deuterated forms of the molecule.

In the classical approximation for the external degrees of freedom of a rigid molecule, assuming that the energy of intramolecular vibrations and the rest of energy are separable,

$$Q_1/Q_1^0 - 1 \approx (1/8\pi^2 V) (Q_{\text{vib}}/Q_{\text{vib}}^0) \int [\exp(-\Phi/kT) - 1] \sin\delta dx dy dz d\delta d\varphi d\psi, \quad (2)$$

where Φ is the potential energy of the interaction between the molecule and the surface of the solid as a function of the Cartesian coordinates x , y and z of the molecule mass-centre and the Euler angles δ , φ , ψ , which determine the orientation of the molecule to the surface, Q_{vib} and Q_{vib}^0 are the vibrational partition functions of the adsorbed molecule and the molecule in the gas phase. Putting (2) into (1) and assuming $Q_{\text{vib}} = Q_{\text{vib}}^0$, we obtain

$$V_{\text{gH}}/V_{\text{gD}} = S_1^{\text{H}}/S_1^{\text{D}}, \quad (3)$$

where the configurational integrals S_1 are given by the expression:

$$S_1 = \int [\exp(-\Phi/kT) - 1] \sin\delta dx dy dz d\delta d\varphi d\psi. \quad (4)$$

If the potential function Φ does not depend on the translational coordinates of the molecule mass-centre parallel to the surface (coordinates x and y) and on the rotational coordinates in the plane parallel to the surface (angle φ), which is approximately correct, for instance, in the case of adsorption on the basal face of graphite, and if we assume that the vibrations of the molecule mass-centre normal to the surface are harmonic, then

$$\Phi = \Phi_0 + (\Phi''_z/2) (z - z_0)^2, \quad (5)$$

where $\Phi_0(\delta, \psi)$ and $\Phi''_z(\delta, \psi)$ are the values of Φ and the second derivative of Φ with respect to the coordinate z at the equilibrium distance $z_0(\delta, \psi)$ of the molecule mass-centre at fixed angles δ and ψ , and

$$S_1/2\pi A = \int (2\pi kT/\Phi''_z)^{1/2} \exp(-\Phi_0/kT) \sin\delta d\delta d\psi. \quad (6)$$

If the system deviates from the classical one, but not significantly, and the quantum corrections can be calculated by the Pitzer and Gwinn approximation³⁶, then

$$V_{\text{gH}}/V_{\text{gD}} = S_1^{\text{H}} v^{**\text{H}}/S_1^{\text{D}} v^{**\text{D}}, \quad (7)$$

where

$$v^{**} = \prod_r \frac{h\nu_r}{kT} \frac{\exp(-h\nu_r/2kT)}{1 - \exp(-h\nu_r/kT)}. \quad (8)$$

Here ν_r is the frequency of the harmonic oscillations of the molecule near the potential minimum for the r -th degree of freedom. The Pitzer and Gwinn approximation however, assumes that the degrees of freedom for which we calculate the quantum corrections are harmonic oscillations.

POTENTIAL FUNCTIONS Φ

In the case of the interaction between a non-polar molecule and the surface of a non-polar solid, *e.g.* graphitised carbon black, the main attractive forces are dispersion forces. In this case the potential functions Φ of the interaction between different molecules and the same adsorbent are mainly determined by the chemical and spatial structure of the molecule, by the electromagnetic properties (polarisability α , diamagnetic susceptibility χ) and by the van der Waals radius r_0 of the molecular force centres.

The average length of the C–D bond is shorter than the average length of the C–H bond by 0.004–0.005 Å^{36–40}, and the polarisability of deuterated molecules is 0.5–1.5% less than the polarisability of the hydrogenated form^{37,41–43}. The van der Waals radii r_0 of the H and D atoms in molecules are apparently equal^{20,44–46}. Therefore the difference in the potential functions Φ of the isotopic molecules is mainly caused by the difference in the lengths of the C–H and C–D bonds and by the difference in the electromagnetic properties of the force centres of the isotopic molecules. In calculating Φ both these factors are taken into consideration. Atoms are assumed as the force centres of the molecules. It is assumed that Φ is equal to the sum of the potential functions φ of the interaction between the atoms of the molecule and the C atoms of the graphite lattice, $\Phi = \sum \sum \varphi$. For the interaction between the C and H atoms of the molecules and the C atoms of the graphite lattice we use the semi-empirical potential functions^{34,47}:

$$\varphi_{C\dots C} = -331 r^{-6} - 513 r^{-8} + 4.52 \cdot 10^4 \exp(-3.57 r), \quad (9)$$

$$\varphi_{H\dots C} = -119 r^{-6} - 227 r^{-8} + 0.86 \cdot 10^4 \exp(-3.57 r), \quad (10)$$

where the distance r between the atoms is in Å and φ is in kcal/mole.

According to the Kirkwood-Müller formula the ratio of the dipole-dipole constants C_1 of the dispersion interaction between the D and H atoms of the molecule and the C atoms of the graphite lattice is

$$\frac{C_1^D}{C_1^H} = \gamma = \frac{\alpha_D}{\alpha_H} \left(1 + \frac{\alpha_H/\chi_H - \alpha_D/\chi_D}{\alpha_D/\chi_D + \alpha_C/\chi_C} \right), \quad (11)$$

where α_H , α_D , α_C are polarisabilities and χ_H , χ_D , χ_C are diamagnetic susceptibilities of the H, D and C atoms. If we assume that the ratio C_2^D/C_2^H of the constants of a dipole-quadrupole interaction is equal to the ratio C_1^D/C_1^H and the rest of parameters (the separation of the atoms at the potential minimum and the constant in the exponential) of the potentials $\varphi_{H\dots C}$ and $\varphi_{D\dots C}$ are the same, then

$$\varphi_{D\dots C} = \gamma \varphi_{H\dots C}. \quad (12)$$

Assuming that the decrease in the polarisability α of the hydrocarbon molecules on the substitution of a D atom for an H atom is due to the smaller polarisability of the D atoms, then on the basis of the experimental results for the systems CH₄–CD₄³⁷, C₆H₁₂–C₆D₁₂^{41,42} and C₆H₆–C₆D₆^{41,42} we obtain that $\alpha_D/\alpha_H \approx 0.98$. The diamagnetic susceptibility χ of deuterated molecules apparently has not been measured. It is assumed that the isotopic substitution does not change α/χ (ref. 26) or χ (ref. 48). Using eqn. 11, we obtain $\gamma = 0.98$ and $\gamma = 0.99$, respectively.

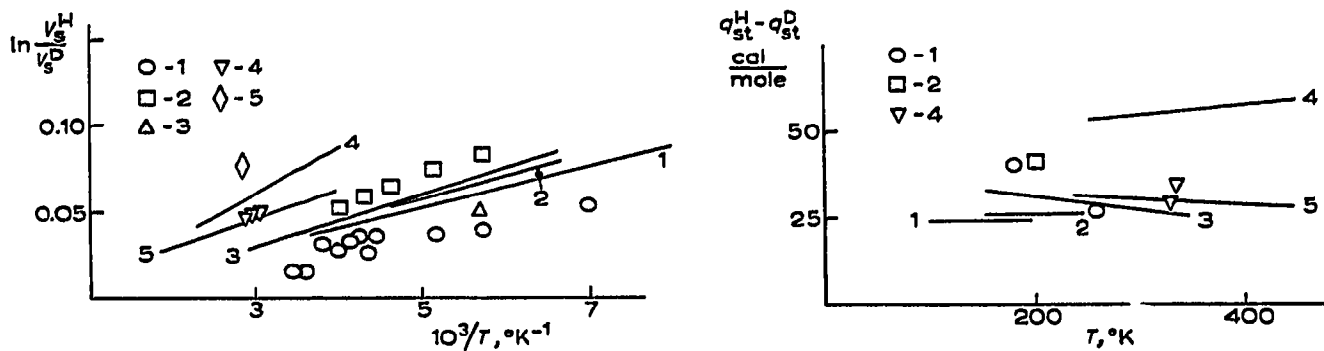


Fig. 1. Calculated (curves) and experimental (points) values of $\ln V_s^H/V_s^D$ for the systems: CH_4-CD_4 (1); $C_2H_6-C_2D_6$ (2); $C_2H_4-C_2D_4$ (3); $C_6H_6-C_6D_6$ (4); and $C_6H_{12}-C_6D_{12}$ (5) as a function of $1/T$.

Fig. 2. Calculated (curves) and experimental (points) values of $q_{st}^H - q_{st}^D$ for the systems: CH_4-CD_4 (1), $C_2H_6-C_2D_6$ (2), $C_2H_4-C_2D_4$ (3), $C_6H_6-C_6D_6$ (4) and $C_6H_{12}-C_6D_{12}$ (5).

In our calculations γ is assumed to be equal to 0.985. The position of the force centre of the D atom, compared with the position of the force centre of the H atom, is assumed to be displaced in the direction of the C atom by 0.004 Å in the CD_4 molecule and by 0.005 Å in the other deuterated molecules.

THERMODYNAMIC QUANTITIES

The calculated values of $\ln V_s^H/V_s^D$ and $q_{st}^H - q_{st}^D$ are compared with the corresponding experimental data^{10,24,25} in Figs. 1 and 2. The calculated curves are fairly close to the experimental data. In contradiction of the experimental data, however, the calculated values of $\ln V_s^H/V_s^D$ for the system $C_2H_4-C_2D_4$ are greater than those for the system $C_2H_6-C_2D_6$; and also the calculated values of $\ln V_s^H/V_s^D$ for the system $C_6H_6-C_6D_6$ are greater than those for the system $C_6H_{12}-C_6D_{12}$. This divergence of calculated values and experimental data can be explained in various ways, for example, it may be caused by neglecting the zero-point energy effect. The contribution of the zero-point energy effect for the systems $C_2H_6-C_2D_6$ and $C_6H_{12}-C_6D_{12}$ can be greater than for the systems $C_2H_4-C_2D_4$ and $C_6H_6-C_6D_6$ because of the greater number

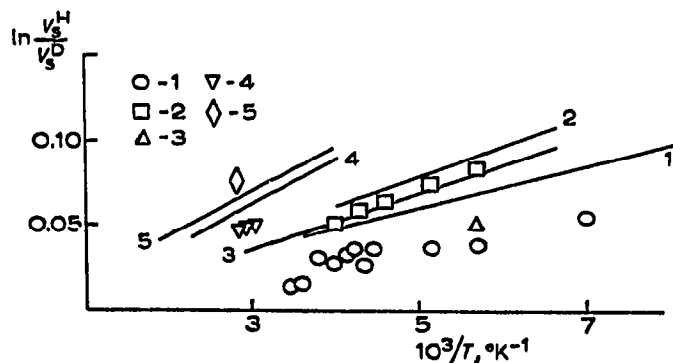


Fig. 3. Calculated (curves) and experimental (points) values of $\ln V_s^H/V_s^D$ as a function of $1/T$. The calculated values are obtained assuming that the position of the force centres of the D and H atoms coincide. The designations are the same as in Fig. 1.

of the substituted H atoms in C_2D_6 than in C_2D_4 , and in C_6D_{12} than in C_6D_6 , as well as the difference of the spatial structure of these molecules. This divergence can also be caused by the errors in the estimation of the differences in the positions of the force centres of the H and D atoms. The variation in the value of this difference hardly changes the results of the calculation for the plane molecules $C_2H_4-C_2D_4$ and $C_6H_6-C_6D_6$, but has a comparatively strong effect on the results for the rest of the molecules. If we assume, that the positions of the force centres of D atom and the H atom coincide, then the calculated curves $\ln V_s^H/V_s^D$ vs. $(1/T)$ (Fig. 3) should have the same sequence as the experimental data. Moreover, the calculated values are very sensitive to the value of the coefficient γ : a change in the coefficient γ of 0.005 causes a change in the values of $\ln V_s^H/V_s^D$ and $q_{st}^H - q_{st}^D$ of 30–50%. Therefore, the above discrepancy between the calculated values and the experimental data can also be caused by small changes in the coefficient γ for these systems.

The translational quantum effect for the isotope substituted hydrocarbon molecules is small: for the system CH_4-CD_4 at 100°K the quantum corrections are equal to -0.016 for $\ln V_s^H/V_s^D$ and -6 cal/mole for $q_{st}^H - q_{st}^D$. The quantum corrections for the rotational degrees of freedom must be added to this effect. However, the calculation of the last effect for the polyatomic molecules is very difficult. Allowance for this effect would lower the calculated values for CH_4-CD_4 slightly. For heavier molecules, not at very low temperatures, the quantum statistical effects for the external degrees of freedom are not significant and may be neglected.

The calculated values of $(\Delta S_a^H - \Delta S_a^D)/R$ are 0.01–0.03.

Thus, the results of the calculations show that the isotopic effect on the adsorption of hydrocarbon molecules on graphitised carbon blacks is mainly caused by the difference of the potential functions Φ of the interaction of isotopic molecules with the surface. The comparison of the calculated values with the experimental data shows that the zero-point energy effect apparently contributes significantly to the isotopic effect for the hydrocarbon molecules. The quantum effects for the external degrees of freedom are only significant in the case of the lightest molecules.

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