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MOLECULAR-STATISTICAL CALCULATION OF RETENTION VOLUMES
IN GAS ADSORPTION CHROMATOGRAPHY

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SUMMARY

The retention volumes, V_R , for a series of hydrocarbons in gas adsorption chromatography on the basal face of graphite at zero surface coverage were calculated by a semi-empirical molecular-statistical method. The potential function of the interaction between a molecule and a surface is assumed to be equal to the sum of the potential functions of the interaction between atoms of the molecule and atoms of the adsorbent. The potential functions of the interaction between the C and H atoms of saturated hydrocarbon molecules and the C atoms of the graphite lattice (the atom-atom potential functions) were estimated by methods according to the theory of the intermolecular interactions and were corrected using experimental adsorption data for methane, ethane and propane on graphitized thermal carbon blacks. The calculated values of V_R for all the saturated hydrocarbon molecules considered (*n*-butane, isobutane, *n*-pentane, neopentane, cyclopentane, *n*-hexane, and cyclohexane) are in good agreement with the experimental values of V_R on graphitized thermal carbon blacks. The calculations of V_R for unsaturated and aromatic hydrocarbon molecules made it possible to estimate the difference between the potential functions of interaction of the C atoms of saturated, unsaturated, and aromatic molecules with graphite.

In the gas adsorption chromatography with small sample sizes the retention volume V_R depends on the structure and the surface area of the adsorbent, the structure of the molecules and the temperature. Therefore the interpretation of experimental data and the development of methods for the prediction of the retention volumes from the structure of the solid and the molecules is one of the main problems in the theory of adsorption chromatography¹. To solve this problem it is necessary to use methods appertaining to statistical thermodynamics and the theory of the intermolecular interactions.

At low (zero) surface coverages the retention volume V_R per unit of surface area can be expressed through the partition function Q of the molecule by the equation²⁻⁴:

$$V_R = \frac{1}{A} \frac{Q - Q^0}{Q^0/V} \quad (1)$$

where A is the surface area of the solid, Q and Q^0 are the partition functions for the adsorbed molecule and molecule in the gas phase, respectively, V is the gas volume.

In the classical approximation for quasi-rigid molecules, *i.e.* for molecules which have no degrees of internal rotational freedom (for instance, molecules of methane, benzene)²⁻⁴

$$V_R = (1/8\pi^2 A) \int [\exp(-\Phi/kT) - 1] \sin\vartheta dx dy dz d\vartheta d\varphi d\psi \quad (2)$$

where Φ is the potential energy of the interaction between the molecule and the surface as a function of Cartesian coordinates of the molecule mass centre (x, y, z) and of the Euler's angles (ϑ, φ, ψ) which determine the orientation of the molecule with respect to the surface.

Most complex molecules have internal rotation. If comparatively stable configurations of the molecular-rotational isomers are formed during internal rotation (for instance, in the case of n -alkane molecules beginning with n -butane), the gas of such molecules can be considered as an equilibrium mixture of the rotational isomers of the molecule. In this approximation⁵

$$V_R = \sum_{i=1}^m x_i V_{R,i} \quad (3)$$

where $V_{R,i}$ is the retention volume for the i th rotational isomer, x_i is the molal fraction of this isomer in the gas phase, m is the number of the rotational isomers.

If the potential barrier for the internal rotation of the molecule is considerably greater than the variation of the potential energy Φ of the interaction between the molecule and the surface during the internal rotation of the adsorbed molecule, and if the molecule does not form rotational isomers during internal rotation (for instance, molecules of ethane, propane, toluene) then in the first approximation the change in the internal rotation of the molecule during adsorption can be neglected. In this case for the calculation of V_R the molecule can be considered as quasi-rigid, *i.e.* eqn. 2 can be used⁶.

Statistical eqns. 1-3 give the relation between V_R and the potential function Φ of the interaction between a molecule and a surface. Solely theoretical calculation of function Φ from the physico-chemical properties of the molecule and the surface of the solid or determination of this function from experimental values of V_R is a very difficult problem. This problem can be significantly simplified if we assume that the potential function Φ of the interaction between a molecule and an adsorbent is equal to the sum of the potential functions l of the interaction between atoms of the molecule and atoms of the solid, *i.e.*

$$\Phi = \sum_i \sum_j l_{ij} \quad (4)$$

where l_{ij} is the potential function of the interaction between i th atom of the molecule and j th atom of the solid (the atom-atom potential function). This approximation is supported by the additivity of the heat of adsorption for linear and planar molecules. When the above approximation is used we must determine the atom-atom potential functions l_{ij} and summarize them taking into account the chemical and geometrical structure of the molecule and the surface.

In the first approximation the form of the atom-atom potential function can be chosen on the basis of the approximate theory of intermolecular interactions.

Buckingham's potential is, apparently, a good approximation to this function in the case of interaction between non-polar molecules and a surface:

$$l_{ij} = -C_{1ij}r_{ij}^{-6} - C_{2ij}r_{ij}^{-8} + B_{ij}e^{-r_{ij}/\rho_{ij}} \quad (5)$$

where r_{ij} is the distance between two interacting atoms, C_1 , C_2 , and B and ρ are parameters. In the first approximation these parameters can be estimated from the physico-chemical properties of the molecule and the solid using various approximate quantum-mechanical formulae and combination rules. Further they can be corrected using experimental values of V_R for some molecules of the same homologous series on a given adsorbent³.

In this way values of V_R for a series of hydrocarbon molecules on the basal face of graphite were calculated. The experimental values of the Henry's constant K_1 determined at different temperatures for adsorption of methane, ethane and propane on thermal carbon blacks graphitized at approximately 3000° were used for the correction of the parameters of the potential functions $l_{C...C}$ and $l_{C...H}$ for the interaction of the C and H atoms of the saturated hydrocarbon molecules with the C atoms of the graphite lattice. The following equations were obtained for the corrected atom-atom potential functions:

$$l_{C...C} = -331r^{-6} - 513r^{-8} + 4.52 \cdot 10^4 \exp(-3.57r) \text{ kcal/mole} \quad (6)$$

$$l_{C...H} = -119r^{-6} - 227r^{-8} + 0.86 \cdot 10^4 \exp(-3.57r) \text{ kcal/mole} \quad (7)$$

where r is distance in Å. The corrected potential functions differ little from those estimated theoretically.

Using these atom-atom potential functions we calculated values of V_R for *n*-butane, isobutane, *n*-pentane, neopentane, cyclopentane, *n*-hexane and cyclohexane.

The calculated values of V_R for molecules of *n*-alkanes are compared with the corresponding experimental values on graphitized thermal carbon blacks in Fig. 1. The calculated values are in good agreement with the experimental ones for all six *n*-alkane molecules studied. The calculated and experimental values of V_R for the

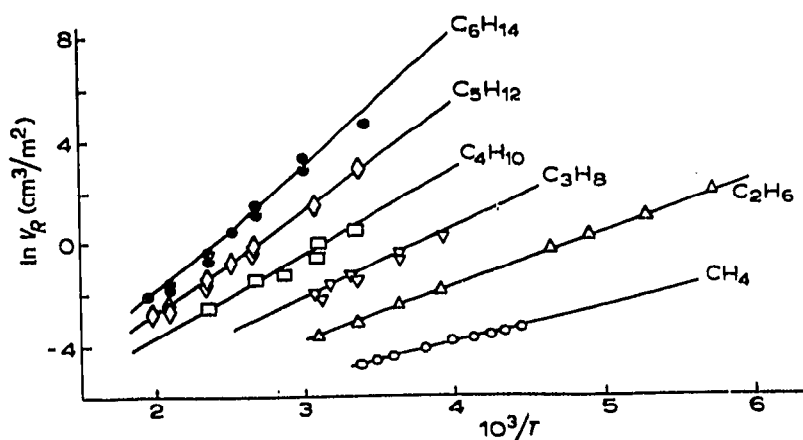


Fig. 1. Calculated (curves) and experimental (points) values of the retention volume as a function of the reciprocal of the absolute temperature for methane, ethane, propane, *n*-butane, *n*-pentane and *n*-hexane.

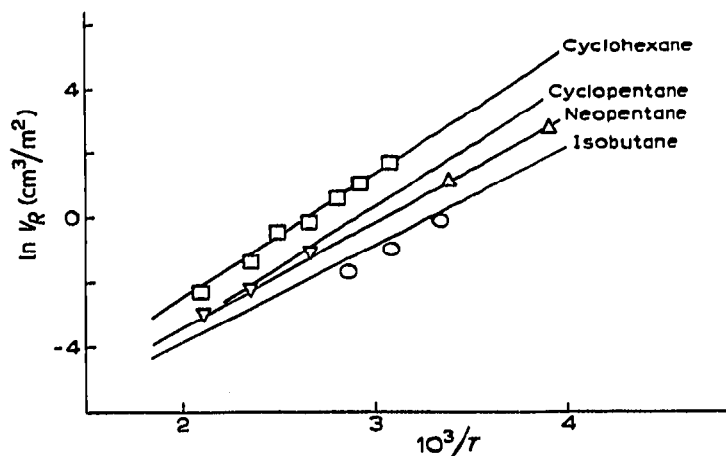


Fig. 2. Calculated (curves) and experimental (points) values of the retention volume as a function of the reciprocal of the absolute temperature for isobutane, neopentane, cyclopentane, and cyclohexane.

structural isomers of *n*-butane and *n*-pentane, *i.e.* for isobutane and neopentane, as well as for the alicyclic compounds—cyclopentane and cyclohexane—are shown in Fig. 2. They are in good agreement also.

So, our calculations showed that the retention volumes in the gas adsorption chromatography for saturated hydrocarbons can be calculated by the molecular-statistical method from the chemical and geometrical structure of the molecules and surface of the solid using the semiempirical atom-atom potential functions.

The state of the electrons of the carbon atoms in unsaturated and aromatic hydrocarbon molecules is somewhat different from that in saturated hydrocarbon molecules. Therefore the atom-atom potential function $l_{C...C}$ for the interaction of the carbon atoms of unsaturated and aromatic hydrocarbon molecules with the carbon atoms of the graphite lattice must be somewhat different from the potential function $l_{C...C}$, eqn. 6, of the interaction between the carbon atoms of saturated hydrocarbon molecules and the carbon atoms of the graphite lattice. To evaluate the magnitude of this effect, the experimental values of V_R for some molecules of

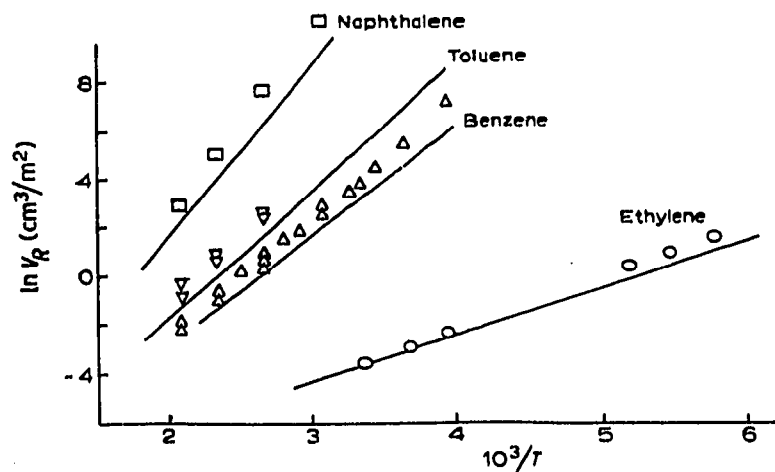


Fig. 3. Calculated (curves) and experimental (points) values of the retention volume as a function of the reciprocal of the absolute temperature for ethylene, benzene, toluene, and naphthalene.

unsaturated and aromatic hydrocarbons were compared with the values of V_R calculated using the same potential function for the interaction between carbon atoms as in the case of adsorption of saturated hydrocarbons. The results are shown in Fig. 3. The experimental values are somewhat greater than the calculated ones for all molecules. This divergence corresponds to the increase of the potential energy of the interaction between the carbon atom and the graphite surface by 0.08 kcal/mole (7%) in the case of unsaturated and aromatic molecules.

In principle, the atom-atom potential functions of the interaction of the carbon atoms of unsaturated and aromatic hydrocarbon molecules with the carbon atoms of the graphite lattice can be determined using experimental data for ethylene and benzene. Furthermore, using these functions the calculations of V_R for any other unsaturated and aromatic molecules can be made. The results apparently are also in good agreement with experimental data as in the case of saturated molecules. The verification of these assumptions is, however, prevented by the absence of the reliable experimental data on adsorption and chromatography of unsaturated and aromatic hydrocarbon molecules on graphitized carbon blacks over a wide range of temperatures. The difference between the potential functions $\mathcal{L}_{C...C}$ for the carbon atoms in saturated, unsaturated and aromatic hydrocarbons is small. The above equations for the atom-atom potential functions can therefore be used for the approximate calculation of V_R for any hydrocarbon molecule on graphitized carbon blacks. The programs developed for the electronic computer permit such calculations to be made fairly quickly.

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