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The Isosteric Heats of Adsorption of Amines on Paraffin and Polyethyleneglycol.

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Abstract Isosteric heats of adsorption of amines on paraffin and polyethyleneglycol were measured by gas chromatography. Values with polyethyleneglycol were significantly higher than those with paraffin due to the N-H···O bonding. The contribution of C-H···O bonding to the isosteric heats of adsorption was negligible. The additional heats of adsorption observed as the sample size increased also increased as the number of amino hydrogen atoms decreased. This tendency was more significant with polyethyleneglycol indicating that strong directing force of amino hydrogen of primary and secondary amines to the surface hinder lateral attractive interaction which could be favored with free orientation.

Introduction

Many workers have determined the isosteric heat of adsorption of hydrocarbons and halogenated hydrocarbons as well as rare gases as adsorbate on graphite and other homotattic adsorbents.[1~6]

Gas chromatographic method has recently been widely used for the measurement of formation constants of nonionic complexes[7,8] hydrogen bond strength and heat of adsorption.[9,10] Vivilecchia and his coworker reported distinct advantages of chromatographic technique over the previous techniques such as spectroscopic and calorimetric and nmr methods for the measurements of hydrogen bonding constants.[11]

A number of works related with isosteric heat of adsorption measured by gas chromatography have testified that the results were in good agreement with the values obtained by calorimetric method. This technique primarily depends on the accurate measurements of retention times of the adsorbate as a function of temperature. A higher degree of accuracy is obtained when the average surface concentration of adsorbed gas in the column is low enough to be within the range described by the Henry's law portion of the adsorption isotherm. The adsorption isotherm according to $\theta=CP$ shows that the adsorbate coverage θ is proportional to pressure P and, regardless of the form of the distribution,

Henry's law yields an isotherm that is a straight line through the origin. Hence, every experimental adsorption isotherm, no matter how heterogeneous the substrate, reduces to Henry's equation where values of θ are low.[12] In general, the more readily condensable the gas, the higher the temperature needs to be for the adsorption to obey Henry's law.

Since no research has yet been reported on adsorption of amines, we intended to make comparative studies between primary, secondary and tertiary amines with respect to their adsorptive natures, particularly to the adsorbents which contain either oxygen or hydrogen, and isosteric heats of adsorption with the aid of gas chromatographic technique. The effects of hydrogen directly attached to the nitrogen and steric hindrance of the molecules and basicity of amines upon their adsorption processes were primary subjects of this study. It is suggested that a desirable adsorbent for the purpose of making these comparisons more accurate could be obtained by using a nearly completely homotattic surface which could be made by uniform coating with non-volatile partitioning liquid such as paraffin and polyethyleneglycol (p. e. g.).

Experiment

The instrument used was Shimadzu gas chromatograph Model GC-1C. The temperature of the column oven is proportionally controlled by a SCR system. The temperatures of the sample injection ports and the outlet of carrier gas are also controlled. Their temperature-settings are made by a direct reading dial. The thermal conductivity detector installed is the high sensitivity hydrogen flame ionization detector and electron capture detector. Three straight stainless columns of 3 mm in diameter and 375 mm long with an aluminum gasket were connected for use.

The diatomaceous earth for the packing was sieved to have the fraction of 40~60 mesh. The diatomaceous earth was coated by paraffin and polyethyleneglycol as partitioning liquid dissolved in a volatile solvent. An amount of the liquids corresponding to 4% of the diatomaceous earth in weight was used. The solvent was evaporated in the oven at the heat of 130°C for over night. Six grams of coated packing material was packed into the column with the aid of a vibrator. The columns were kept sealed when not beening used and exhibited no change in behavior with time. The dehydrated nitrogen gas obtained by passing through the cylinder which contained a strong dehydrating agent was used as carrier gas.

Sample injection was made by a micro syringe by inserting the needle of the syringe through the silicone rubber septum of the sample port and injecting the reproducible pulse volumes of 0.5, 1, 1.5, 2, and 2.5 μl. of each amine. Each precise injection volume was measured by means of peak cutting method. To get rid of surface accumulation due to somewhat irreversible adsorption at the moment 20 minutes was allowed to elapse before the next injection was made. The flow rate (cm^3/sec) was measured by the installed soap film flow meter at room temperature. In all of this work the measurements of each adsorbate at the temperature between 60–150°C with the intervals of 10°C were repeated six times. The relative errors of the measured retention times were within ± 1 second. The measured retention time was corrected by using helium as a reference gas. The The true retention time of the adsorbate was then obtained as the difference between the observed retention times of adsorbate and reference gas. The true retention times of each adsorbate at the lowest coverage, $\theta=0$, were obtained by graphical extrapolation at each temperature.

Propyl amine, diethyl amine and tertiary butyl amine were analytical reagents supplied by Kisida, Kagaku Co. Osaka. *n*-butyl amine, triethyl amine and the partitioning liquids were from Wako Pure Chemical Industries L. T. D. Most of the amines were redistilled and the purities were checked by gas chromatography before use.

The calculation was made by utilizing the equation:

$$\text{Lim}\, q^{st}=R[d\ln(F,t)/d(1/T)] \qquad (1)$$

where F_r and t refer to flow rate at room temperature and true retention time. The correct dependence of retention time on the parameters as predicted by the equation (1) has been already verified.[13] The plot of ln (F,t) versus $1/T$ should, therefore, be a straight line whose slope equals q^{st}/R.

Result and discussion

Even when the sample size was extremely small as long as it was made very carefully with sufficient accuracy and the fluctuation of operational conditions are controlled, we found satisfactory reproducibilities in the peak area as well as retention times of chromatogram. The measured retention times of the adsorbate as a function of temperature show straight line through the origin. Nearly symmetrical elution peaks show the best conditions of low substrate heterogeneity.

The limiting isosteric heats of adsorption of amines adsorbed on the paraffin or p. e. g. were calculated by the equation (1). The isosteric heats of adsorption of amines on p. e. g., $q^{st}{}_{pe}$ in the *Table* I, is significantly higher than those on paraffin, $q^{st}{}_{pa}$. It is clear that the difference between these two, Δq^{st}, is related to the number of amino hydrogen atoms and the difference between the surface constitution of the substrates. The effect of amino hydrogen on adsorption of amines on the surface of p. e. g. which contain oxygen uniformly distributed is obviously pointing out the important role of N—H···O bonding over the entire adsorption processes. In considering the relatively larger values of Δq^{st} of propyl and *n*-butyl amine whose steric hindrances are negligible, the heat of hydrogen bond formation per bond should be nearly 2 Kcal/mol assuming the nitrogen atom of amine acts equally on either substrate. In fact this assumption is verified by comparing the values of triethyl amine. And the contribution of hydrogen bonding to the heat of adsorption is roughly expressed by the relative value of $\Delta q^{st}/q^{st}{}_{pe}$.

Table I. The limiting isosteric heats of adsorption (Kcal/mol) of adsorption of amines on paraf. and p. e. g.

amine	temp. range(°K)	$q^{st}{}_{pa}$	$q^{st}{}_{pe}$	Δq^{st}	$\Delta q^{st}/q^{st}{}_{pe}$
propyl amine	335—386	5.48	9.80	4.32	0.44
n-butyl amine	350—395	6.23	10.43	4.20	0.40
tert. butyl amine	330—380	5.90	8.74	2.84	0.33
diethyl amine	330—380	7.68	8.94	1.26	0.14
triethyl amine	368—400	7.10	7.23	0.13	0.02

From the difference between the value of $q^{st}{}_{pa}$ of propyl amine and that of *n*-butyl amine, contribution of q^{st} per —CH_2— group should be about 0.7Kcal/mol. Similar results obtained by the difference between $q^{st}{}_{pe}$ of propyl amine and $q^{st}{}_{pe}$ of *n*-butyl amine indicate that C—H···O bonding is negligible in the process of

adsorption.

The slight decrease in q^{st} per hydrogen bond of tertiary butyl amine and diethyl amine might be primarily caused by the increment of electron density of the hydrogen atom, d_H, which is calculated by the two center Hückel method and shown in the *Table* II, polarizability of the adsorbates and steric factor.

Table II. Calculated electron densities and reference data for amines

amine	*M. W.*	*B. P.*	PK_b	d_N[a]	d_H
$C_3H_7NH_2$	59.11	49°C	3.420	3.5281	0.7814
$C_4H_9NH_2$	73.14	78 〃	3.387	3.5281	0.7814
$(CH_3)_3CNH_2$	73.14	46 〃	—	3.5323	0.7815
$(CH_3CH_2)_2NH$	73.14	55 〃	3.022	3.3566	0.7998
$(CH_3CH_2)_3N$	101.19	89 〃	3.258	3.2052	—

[a]Calculated electron density of nitrogen atom according to the two center Hückel method.[14]

It is not clear whether the electron density of the nitrogen atom is related with the values of $q^{st}{}_{pa}$ or $q^{st}{}_{pe}$. However, it is clear that the order of $q^{st}{}_{pa}$ follows the order of pK_b of amine This is attributed to the fact that the isosteric heat of amines depends on charge density of the

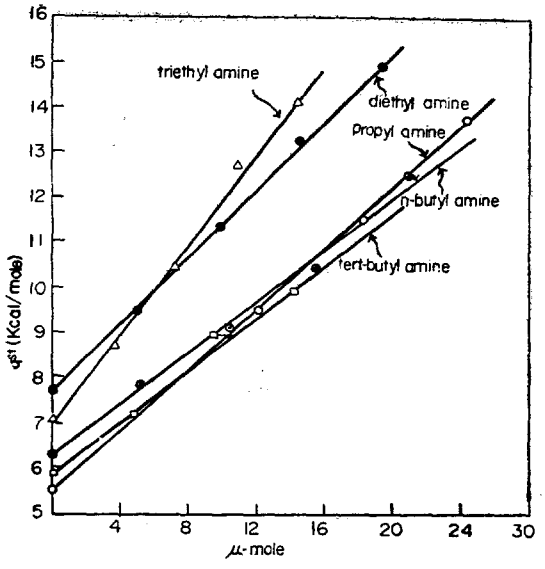

Fig. 1. Plots of q^{st} against μ-mole of amines, injected to the paraffin coated adsorbent

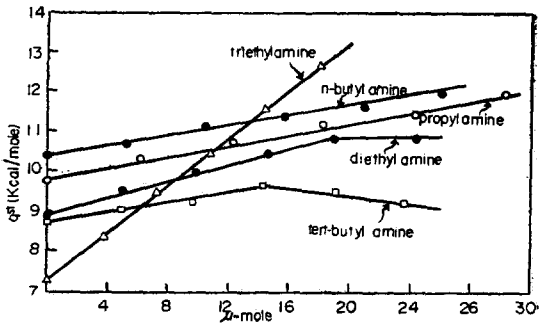

Fig. 2. Plots of q^{st} against μ-mole of amines, injected to the polyethyleneglycohol coated adsorbent.

hydrogen atom attached to the nitrogen atom.

The symmetric peaks of chromatogram with various sample sizes from 0.5 to 2.5μl. can be interpreted with assurance for near homotattic substrate and performance of Henry's adsorption within the given surface concentration.

The increment of q^{st} due to the increasing sample size which is directly correlated with the surface concentration and fraction of the whole surface of adsorbent covered by an adsorbed layer, θ, is attributed to the additional adsorption potential energy due to molecules already adsorbed. Depending on how many molecules are adsorbed on the total surface, the additional adsorptive potential becomes important. The positive slopes of the q^{st} as a function of θ or sample size were interpreted as a result of additional interaction, namely lateral attraction, between the adsorbates. The negative tendency was ascribed to repulsive interaction such as between induced dipole moment of the molecule, which thereby decreases the attrative interaction forces.[15]

However, the concept of repulsive interaction due to the exclusive area occupied by the molecule and attractive interaction, involved in any adsorption process at same time, was proved by de Boer with the equation,[16]

$$P=2\alpha\theta/\beta.$$

Table III. The additional adsorptive potential P (Kcal/mol/μ-mole) and its ratio.

amine	P_1 (paraf.)	P_2 (p. e. g.)	r_{P_1} [a]	r_{P_2}
propyl amine	0.333	0.068	0.66	0.23
n-butyl amine	0.258	0.059	0.51	0.20
tert. butyl amine	0.295	0.061	0.58	0.20
diethyl amine	0.376	0.105	0.74	0.35
triethyl amine	0.507	0.299	1.00	1.00

a: the ratio of P_i of other amine devided by P_1 of triethyl amine which has relatively simpler conformation.

He also expressed the constants α and β for spherical isotropic molecules by van der Waals constants,

$$\alpha/\beta=a/2b.$$

In these two equations it is shown that the additive interaction potential should be proportional to the attractive interaction potential and inversely proportional to the molecular size. For the non-spherical molecules we shall now make use of the following equations,

$$q^{st}=q_{\theta}^{i\,t}{}_{=0}+P \qquad (2)$$

$$P=\frac{(k+a)}{A}M \qquad (3)$$

where A and a refer respectively to parameter related to molecular area and van der Waals constant and M and k stand for sample size in μ-mole and additional attractive potential besides besides intermolecular force due to the dispersion energy which is already expressed by van der Waals constant a.

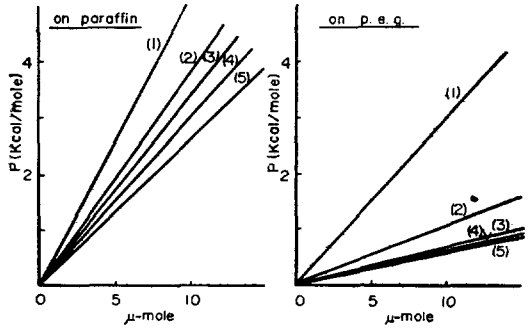

Fig. 3 Linear plots of additional adsorption potential *vs* sample size: (1) triethylamine, (2) diethylamine, (3) propylamine, (4) tert-butylamine, (5) *n*-butylamine

The relative ratio r_{P_1} and r_{P_2} in the *Table* III show the appropriate tendencies of attracive interaction potential increase inversely with the number of hydrogen atoms attached to the nitrogen atom. From *Fig.* 3, this tendency is more obvious when the amines are adsorbed on p. e. g. which allows strong N—H···O bonding. Including the result discussed previously, this fact is interpreted as the restricting effect of amino hydrogen, directing the molecule from a freely oriented arrangement to the surface. The relative ratio in the *Table* III was compared with the ratio calculated by the equation derived from the equation (3)

$$P_{ps}/P_t=\frac{(k_{ps}+a_{ps})}{(k_t+a_t)}\cdot\frac{A_t}{A_{ps}} \qquad (4)$$

where t is tertiary amine and ps is primary or secondary amine. The estimated relative ratio applying the surface area for various probable conformations and arrangements, roughly indicated the increasing tendency of k in order of $k_t>k_s>k_p$. This fact is roughly interpreted as the contribution of amino hydrogen on lateral interaction between the neighboring adsorbates.

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