

Adsorption Characteristics of Elemental Iodine and Methyl Iodide on Base and TEDA Impregnated Carbon

Hoo Kun Lee and Geun Il Park

Korea Atomic Energy Research Institute

(Received August 28, 1995)

활성탄을 이용한 원소요오드 및 유기요오드 흡착특성

이후근 · 박근일

한국원자력연구소

(1995. 8. 28 접수)

Abstract

For the purpose of controlling the release of radioiodine to the environment in nuclear power plants, adsorption characteristics of elemental iodine and methyl iodide on the base carbon and 2%, 5% TEDA impregnated carbons were studied. The amounts of adsorption of elemental iodine and methyl iodide on the carbons were compared with Langmuir, Freundlich, Sips and Dubinin-Astakhov(DA) isotherm equations. Adsorption data were well correlated by the DA equation based on the potential theory. Adsorption energy distributions were obtained from the parameters of the DA equation derived from the condensation approach method. For the adsorption of methyl iodide and elemental iodine-carbon system, the DA equation can be well expressed by the degree of heterogeneity of the micropore system because the surface is nonuniform when its potential energy is unequal. The adsorption energy distribution was investigated to find a surface heterogeneity on the carbon. The surface heterogeneity for iodine-carbon system is highly affected by the adsorbate-adsorbent interaction as well as the pore structure. The surface heterogeneity increases as a content of TEDA impregnated increases. The adsorption nature of methyl iodide on carbon turned out to be more heterogeneous than that of elemental iodine.

요 약

원자력발전소에서 방사성 요오드를 제거하기 위해 사용되는 원료활성탄과 2%, 5% TEDA(Triethylene-Diamine) 침착활성탄을 이용하여 원소요오드와 유기요오드인 메틸요오드에 대한 흡착특성을 분석하였다. 여러 흡착 등온식을 선정하여 실험치와 비교함으로써 선정된 흡착 등온식의 적합성 여부를 검증하였다. 흡착평형 실험결과 Dubinin-Astakhov(DA) 등온식이 여러 가지 흡착등온식 가운데 가장 적합한 것으로 나타났다. 흡착표면의 흡착에너지 분포가 불균일(Heterogeneous)하기 때문에 포텐셜(Potential) 에너지를 근거로 하는 DA 등온식이 흡착평형 관계를 보다 정확하게 나타내는 것으로 생각된다. 흡착표면의 불균일성을 확인하기 위해 흡착에너지 분포도를 원료활성탄과 침착활성탄에 대해 상

호 비교하였다. 활성탄-요오드 흡착시스템에서 불균일성은 활성탄의 기공구조 뿐만 아니라 흡착질과 활성탄과의 상호관계에 의해서도 영향을 받게된다. 따라서 흡착표면의 불균일성은 활성탄을 침착함에 따라서 증가하게 되고 원소요오드보다 유기요오드의 경우 불균일성이 더 커지는 것으로 보여진다.

1. Introduction

During the irradiation of nuclear fuel in power plants, various hazardous radioactive materials are produced. Controlling the release of these radioactive materials to the environment has become an important topic. Among these products, it is widely recognized that radioiodines are the most important nuclides due to their volatility and the significant radiological effects on the human body[1]. Airborne iodine in the gaseous effluent has the different chemical forms such that elemental iodine(I and I_2), organic iodide (CH_3I) and hypiodous acid (HOI) may be present in significant amounts[1, 2]. The control of these species depends on the design of the off-gas treatment and ventilation systems within each particular plant and also on the reactor type.

The removal of iodine from the gaseous effluent of nuclear power plant has been performed using impregnated activated carbon[2, 3]. Particularly, the retention of methyl iodide were improved by impregnation of activated carbon[2-5]. Iodine salts(a mixture of KI and I_2)[2], triethylene-diamine (TEDA) [2-4], and a mixture of the two, were generally used for this purpose. Tertiary amine-impregnated carbons have been originally developed for the control of various halide-type toxic gases to form the stable quaternary salts on the surface of activated carbon[6]. Their use to control the organic radioactive halides, especially CH_3I^{131} , has been introduced by Collins et al[7]. Among these halide complexing amines, TEDA is widely used in the world for nuclear facility air cleaning[3, 4].

Adsorption isotherms describe the equilibrium relationship between the concentrations of adsorbed and bulk phase at a given temperature. Several equations, theoretically and empirically based, have been used to describe the relationship between the

concentration adsorbed onto a surface and the equilibrium concentration in the bulk phase. Those equations also can be used to provide information about adsorption energies at gas-solid surface and sorption capacities of the solid.

The Langmuir equation[8] has been proven to adequately describe the adsorption of gases in many instances. There are five assumptions inherent in the Langmuir sorption equation : (1) the adsorbed gas behaves ideally, (2) the adsorbed layer is a monolayer, (3) the surface is homogeneous, (4) there is no lateral interaction between adsorbed gases, and (5) adsorbed molecules are fixed and do not move on the surface. At low concentrations, the first two assumptions generally hold. However, in most natural systems, the last three conditions are seldom fulfilled. Nevertheless, the Langmuir isotherm has been found to adequately describe the adsorption in many instances[9-12]. However, the Langmuir equation is not generally useful in describing adsorption in heterogeneous systems because of its intrinsic assumption of homogeneous sorption sites. The Freundlich equation, usually assumed to be empirical[13], can be derived from an adsorption model where the adsorption energy decreases exponentially as the amount of adsorbed molecules increases. However, the Freundlich equation does not satisfy the required limiting cases such as the Henry's law at low concentrations near zero and the finite adsorption capacity [14]

According to the Freundlich isotherm, the amount adsorbed will increase indefinitely with concentration. Therefore Sips equation is superior for data correlation covering wide ranges of concentrations and temperatures, when both Langmuir and Freundlich isotherms fail[15].

In this work, the Dubinin-Astakhov(DA) equation is selected as a single species isotherm for following

merits; (1) good fit of data over wide concentration ranges, (2) good temperature correlation, (3) easy evaluation of the adsorption energy distribution. The DA equation can be regarded as a hybrid between the Dubinin-Radushkevich (DR) isotherm and the Freundlich isotherm [16].

The present work is concerned with the adsorption of iodine such as elemental iodine (I_2) and methyl iodide (CH_3I) onto base carbon and 2%, 5% TEDA impregnated carbons. The objectives of this study are to examine the adsorption characteristics of elemental iodine and methyl iodide on the base carbon and 2%, 5% TEDA impregnated carbons and to obtain the acquisition of valuable information on adsorption equilibrium and adsorption energy distribution. This information can be used to analyze and simulate the adsorption capacity of carbon filter used the off-gas treatment system in nuclear power plant.

2. Adsorption Isotherms

There are various isotherm equations for single-gas adsorption. Here, equilibrium data will be correlated by the Langmuir, the Freundlich, the Sips, and the Dubinin-Astakhov (DA) equations.

$$q = \frac{q_m bc}{1 + bc} : \text{Langmuir} \quad (1)$$

$$q = Kc^{\frac{1}{n}} : \text{Freundlich} \quad (2)$$

$$q = \frac{q_m bc^{1/n}}{1 + bc^{1/n}} : \text{Sips} \quad (3)$$

$$q = q_m \exp \left\{ - \left(\frac{RT}{E} \ln \frac{c_s}{c} \right)^r \right\} : \text{DA} \quad (4)$$

The simplest and still the most useful isotherm, for both physical and chemical adsorption, is the Langmuir isotherm. This isotherm equation is based on the concept of dynamic equilibrium between the rates of condensation (adsorption) and evaporation (desorption). Since the sites already occupied are no longer

available for adsorption, the rate of adsorption per unit surface area is equal to $\alpha \nu (1 - \theta)$, where ν is the collision frequency of gas molecules striking the surface, α is the sticking probability or accommodation coefficient for adsorption, and θ is the fractional coverage.

In Langmuir's original paper [8], adsorption on "amorphous" surface is considered and the amount adsorbed is summed over all types of sites, each having its corresponding value of b , meaning corresponding bond energy or heat of adsorption. According to the Freundlich isotherm, the amount adsorbed will increase indefinitely with pressure [15].

The DA isotherm derived from the potential theory has found to be useful for interpreting adsorption by capillary condensation or pore filling. This isotherm is especially useful for analyzing the adsorption nature on microporous materials such as activated carbons. However, since the characteristic curve according to the potential theory is assumed to be independent of temperature, which applies to adsorption by the temperature-independent dispersion forces. This theory is general so that it can be interpreted the multilayer adsorption characteristic on energetically nonuniform surfaces [15].

The DA equation has an empirical basis confirmed by a large number of experiments. Its drawback from a theoretical point of view is the fact that it contains a free energy instead of a true adsorption energy. However, it is possible to link this equation to a simple theoretical model, which allows a formal description of its basis and parameters. The mean energy of adsorption (more correctly, sorption) E is the free energy of transfer of 1 mol of concentration from infinity (bulk phase) to the surface of the adsorbent [17]. It has also been interpreted as the most probable adsorption energy on the heterogeneous surface of the adsorbent.

The exponent r in Eq.(4) is linked to the degree of heterogeneity of the microporous system, as suggested by the adsorption of various molecules. The energy distributions were calculated according to Eq.(4)

for one value of E and different values of r . These distributions become sharper as r increase which implies a decrease in the energetic heterogeneity of the adsorbent surface.

3. Adsorption Energy Distribution

Adsorption theories on the gaseous phase usually assume the adsorbent surface to be homogeneous, whereas, in reality, most adsorbent surfaces are energetically heterogeneous.

The surface heterogeneity generally plays an important role in the adsorption on solid[18]. The energetic state of an adsorbate molecule depends on its contact point with the solid surface. The interactions of these sites with the adsorbate molecules depend on the chemical nature of adsorbate. i.e., a functional group on the surface may interact strongly with a molecule of one adsorbate and/or weakly with a molecule of another adsorbate. The adsorption energy ϵ , which is greater than zero, is defined as the minimum value of the potential of the adsorbate molecule. For a homogeneous adsorbent the adsorption energies of all adsorption sites are identical, i.e., they are independent of the contact-point of an adsorbate molecule with the solid surface. For a heterogeneous adsorbents, the adsorption energy of a given molecule depends on its position on the solid surface. The adsorption energy ϵ is used generally to define the energetic heterogeneity of adsorbents in the adsorption of single gas. Also, the adsorption energy ϵ is usually defined as a difference between the minimum energy of the gas-solid adsorption potential on the site ϵ^* (micropore) and the vibrational energy.

Adsorbent surfaces are generally classified into homogeneous and heterogeneous ones. When the adsorption energy(potential) $\epsilon(x, y, z)$ is a function only of the distance z from the adsorbent surface, we say that the surface is homogeneous and uniform. If $\epsilon(x, y, z)$ is, at a given distance z from the adsorbent surface, a periodic function of the vector of displacement parallel to the surface from point(x_0, y_0), corre-

sponding to the active site(adsorption center), then, that the surface is homogeneous. In the case when the above mentioned function does not exist, the surface is considered as heterogeneous. However, the terms uniformity and homogeneity as well as non-uniformity and heterogeneity of the adsorbent surface are often used as synonyms.

The adsorbent surface is composed of energetically homogeneous sectors(patches) within which adsorption conditions are identical. Every sector must have a surface area large enough to permit the neglect of interactions of molecules adsorbed at neighbouring homogeneous patches. Most investigations of gas adsorption on heterogeneous adsorbent surface are based on the integral equation of the adsorption isotherm with an adsorption energy distribution $\chi(\epsilon)$ for constant temperature :

$$\theta_t(P) = \int_{\epsilon_0}^{\epsilon_{\max}} \theta(p, \epsilon) \chi(\epsilon) d\epsilon \quad (5)$$

where $\theta_t(p)$ is the total adsorption in terms of adsorbent surface coverage, $\theta(p, \epsilon)$ is the adsorption isotherm for an arbitrarily chosen homogeneous patch of surface area of adsorption energy ϵ and is referred to as the local adsorption isotherm, $\chi(\epsilon)$ is the adsorption energy distribution function characterizing the energetic heterogeneity of the adsorbent surface and the limits of the energy domain, in particular the lower bound ϵ_0 , reflect real physical properties of the system. Eq.(5) is the fundamental equation in the theory of adsorption on heterogeneous solid surface.

Energy distribution function, which is called the differential distribution of adsorption energy, is defined as the derivative of the number of adsorption sites with respect to the adsorption energy. This function has been accepted as a quantitative characteristic of the adsorbent surface, where $\chi(\epsilon)d\epsilon$ is the fraction of the surface with adsorption energies between ϵ and $\epsilon + d\epsilon$. $\chi(\epsilon)$ is the continuous energy distribution normalized to unity from physical considerations :

$$\int_0 \chi(\epsilon) d\epsilon = 1 \quad (6)$$

The integral region Ω is over all possible adsorption energies. When the total adsorption is described by the function $\theta(p)$ and should equal to the moonraker capacity[19], Eq.(5) has no analytical solution; in fact, it has an infinite number of oscillatory solutions and restrictions must be imposed to obtain a solution which has a physical sense.

The energetic heterogeneity of the adsorbent surface estimated by this equation reduces to an analytic or numerical solution with respect to the $\chi(\epsilon)$ function, having assumed the local adsorption model(adsorption in the homogeneous surface sector).

The problem of solving integral Eq.(5) can be simplified by using a variational technique called the condensation approximation(CA). Eq.(5) leads to

$$\theta_i(P) = \int_{\epsilon}^{\infty} \chi(\epsilon) d\epsilon \quad (7)$$

The adsorption energy distribution function becomes

$$\chi(\epsilon) = \frac{d\theta_i(\epsilon)}{d\epsilon} \quad (8)$$

Using the condensation approach (CA) method, the DA equation corresponds to the following energy distribution[17]:

$$\chi(\epsilon) = \frac{r(\epsilon - \epsilon_k)^{r-1}}{E^r} \exp\left\{-\left[\frac{\epsilon - \epsilon_k}{E}\right]^r\right\} \quad (9)$$

The energy distributions become sharper as r increase, which implies a decrease in the energetic heterogeneity of the adsorbent surface.

Experimental studies have confirmed the usefulness of the adsorption isotherm equation for the determination of the heterogeneity of the adsorbent surface. The adsorption energy distributions for elemental iodine and methyl iodide on various carbons were obtained from the parameters of the DA equation.

4. Experimental

The base carbon used in this study was supplied

by Sam Chul Ri Carbon Co(KOREA) and 2%, 5% TEDA impregnated carbons were made by impregnating with chemical reagents on the base carbon in this experiment according to the standard method [7]. For the equilibrium isotherm experiment, the carbon were sieved to give the fraction of a 8–16 mesh particle size. The physical properties of these carbons measured by BET method are listed in Table 1. Approximately 95% of the total surface area was present in pores of less than 15 angstrom according to the results of BET measurement. The impregnation ratio was measured by weight gain and confirmed by spectrophotometric measurement after extraction with the acetonitrile solvent. Physical properties of the adsorbent used are listed in Table 1.

All experiments were carried out in a typical fixed-bed system. The vapors of elemental iodine and methyl iodide were produced from an iodine generator column packed with molecular iodine crystal and a liquid methyl iodide tank through a constant temperature saturator. The gaseous concentrations were adjusted by controlling the temperature of the saturator and the air flow rate flowing the iodine and the methyl iodide generators. Dry air was used as a carrier fluid. The adsorption column, buffer vessel, and gas flow lines were made of glass to prevent the elemental iodine plate-out and methyl iodide trapping. All the experiments were performed at a con-

Table 1. Physical Properties of Carbons Used in This Study

Physical properties	Base carbon	2% TEDA impregnated	5% TEDA impregnated
Surface area (m ² /g)	1,483	1,371	1,275
Pore volume (cc/g)	0.767	0.723	0.658
Bulk density (g/m ³ bed)	4.1×10 ⁵	4.2×10 ⁵	4.3×10 ⁵
Particle radius (m)	7.7×10 ⁻⁴	7.7×10 ⁻⁴	7.7×10 ⁻⁴
Bed void fraction	0.46	0.46	0.46

Table 2. Experimental Conditions for Iodine and Methyl Iodide Adsorptions

Adsorbent	Adsorbate	Input conc. (mol/m ³)	Bed depth (m)	Gas velocity (m/sec)	Adsorption amount (g/g-Carbon)
Base carbon	I ₂	0.00005	0.0056	0.572	0.788
		0.00021	"	"	0.952
		0.00031	"	"	1.019
		0.00048	"	"	1.150
		0.0005	"	"	1.134
		0.0025	"	"	1.288
		0.0113	"	"	1.299
		0.0121	0.017	0.381	1.301
		0.0157	0.084	0.381	1.341
	CH ₃ I	0.0033	0.034	0.596	0.067
		0.0062	"	"	0.098
		0.0181	"	"	0.176
		0.0375	"	"	0.243
		0.0652	"	"	0.348
		0.076	"	"	0.383
		0.087	"	"	0.430
		0.099	"	"	0.423
		0.155	"	"	0.490
		0.343	"	"	0.679
		0.46	"	"	0.775
		0.923	"	"	0.906
2% TEDA impregnated	CH ₃ I	0.003	0.033	0.596	0.083
		0.042	"	"	0.294
		0.06	"	"	0.333
		0.064	"	"	0.346
		0.079	"	"	0.375
		0.137	"	"	0.441
		0.14	"	"	0.498
		0.329	"	"	0.670
		1.79	"	"	0.929
		2.09	"	"	0.932
5% TEDA impregnated	CH ₃ I	0.002	0.032	0.596	0.123
		0.0045	0.032	"	0.162
		0.065	"	"	0.394
		0.074	0.112	"	0.397
		0.258	0.032	"	0.593
		0.301	"	"	0.606
		0.404	"	"	0.672
		0.831	"	"	0.759
		1.81	"	"	0.814

stant temperature of 30°C, and all parts of the system were lined with a water jacket. Water was circulated through this jacket to maintain the temperature of the adsorber. The adsorption column was made of a glass pipe, 2.2cm for elemental iodine adsorption experiment and 1.76cm for methyl iodide in diameter and 30cm long. The height of the packed section was normally 3~10 cm.

The gas scrubbing method was used to analyze the elemental iodine concentration. The effluent iodine vapor flowed into the gas scrubbing bottle contained KI aqueous solution and dissolved in I⁻ chemical form. In order to obtain the high solubility of iodide in KI aqueous solution, Na₂S₂O₃ was used as an additive. The virtue of Na₂S₂O₃ as an additive is to make the complete reaction of iodine to iodide ion in the scrubbing solution. An ion analyzer was used to measure the iodide ion concentration by the help of calibration curve. The ion concentration of absorbed iodide was calculated from the difference between the total iodide concentration and the initial iodide concentration, and this concentration of iodide ion was converted to elemental iodine vapor concentration in gas stream.

A gas chromatography with a flame ionization detector was used to analyze the methyl iodide concentration from the bed effluent. Samples were taken and injected into the injector every 5min by a 6-port gas sampling valve with an electric valve actuator. The experimental conditions and typical results are summarized in Table 2.

5. Results and Discussion

The adsorption isotherms of elemental iodine and methyl iodide were measured dynamically at a constant temperature of 30°C. In this study, single-species equilibrium data were correlated by the two-parameter isotherm equations such as the Langmuir, the Freundlich, the sips and the DA with the three-parameter. In principle, one can obtain the values of the isotherm parameters by minimizing the

mean percent deviation between experimental and predicted values of q (amount adsorbed) defined as :

$$\text{dev}(\%) = \frac{100}{N} \sum_{k=1}^N \left[\frac{|q_{\text{exp}} - q_{\text{pre}}|}{q_{\text{exp}}} \right]_k \quad (10)$$

The percent deviations obtained from each isotherm are summarized in Table 3 and the adsorption isotherm data for base and TEDA impregnated carbons are plotted in Figs. 1-4. The adsorption amount of methyl iodide in low concentration range have no relation with the impregnation ratio on the carbon. On the otherhand, it was observed that the maximum adsorption amount of methyl iodide decreases with increase in that ratio, i.e. it increases in the order of 5% TEDA impregnated carbon < 2% TEDA impregnated carbon < base carbon. This implies that chemisorption dominates at low adsorbate concentrations because of impregnation, but that physical adsorption becomes dominant as the adsorbate concentration increases. The decrease in the maximum amount of adsorption with the increase of impregnation ratio may be the result of the decrease in pore volume(see Table 1).

Among four equations, the DA equation gives the best fit, because this equation contains three adjustable parameters. The Langmuir equation gives the worst result. Such a result implies, in principle, that the adsorption of elemental iodine and methyl iodide onto carbon surface is considered to be quite heterogeneous. It has been known that the surface heterogeneity in carbons is usually due to structural irregularities of pores.

Traditionally, the quantitative estimation of adsorption amount on microporous adsorbents is based on the DA equation since it has a variable heterogeneity parameter, r . Table 3 shows the parameters of the DA equations, q_m , E , and r . When r becomes 1, the DA equation becomes the Freundlich equation which may be derived from an exponential distribution of adsorption energy and the Langmuir-type local isotherm[16] and when r becomes 2, it becomes the Dubinin-Radushkevich(DR) isotherm equation. The value of r has been used as a measure of pore struc-

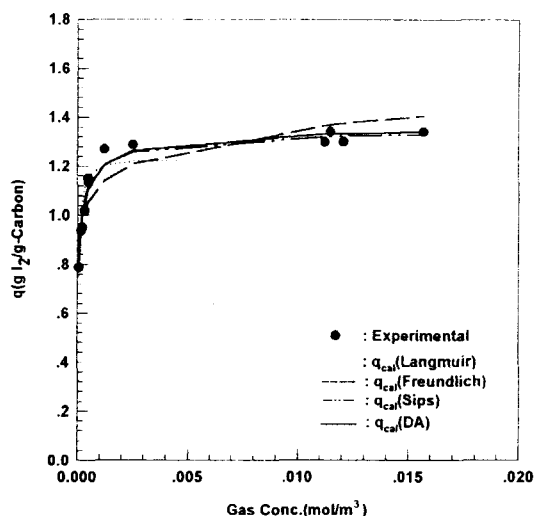


Fig. 1. Equilibrium Adsorption Isotherm of Elemental Iodine on Base Carbon at 30°C.

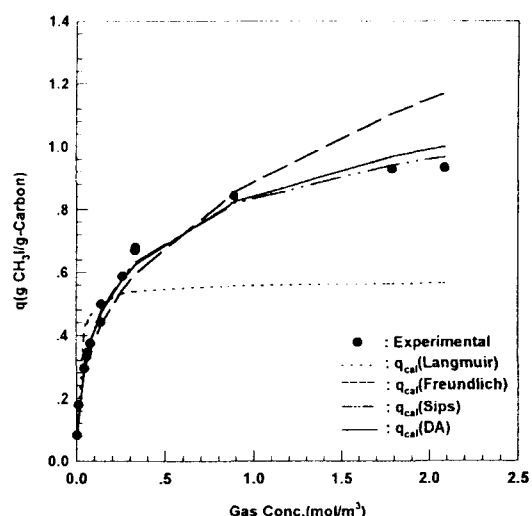


Fig. 3. Equilibrium Adsorption Isotherm of Methyl Iodide on 2% TEDA Impregnated Carbon at 30°C.

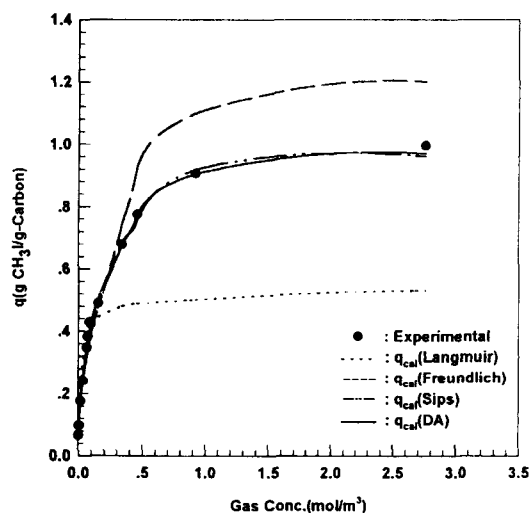


Fig. 2. Equilibrium Adsorption Isotherm of Methyl Iodide on Base Carbon at 30°C.

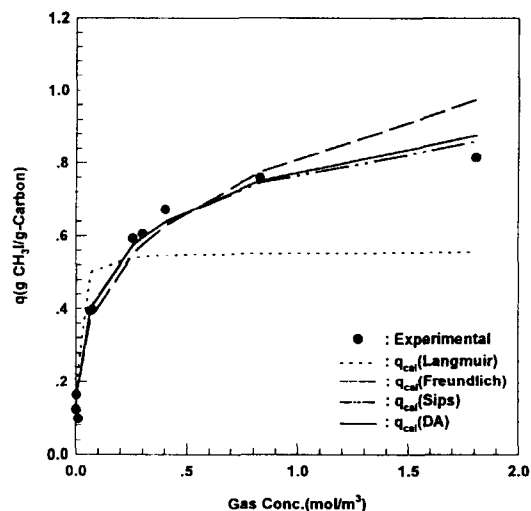


Fig. 4. Equilibrium Adsorption Isotherm of Methyl Iodide on 5% TEDA Impregnated Carbon at 30°C.

ture. In general, it appears that $1 < r < 2$ refers to adsorbents with large micropores and $r > 2$ implies that the adsorbent has very fine micropores[17]. The values of r for elemental iodine(inorganic) and methyl iodide(organic) on base carbon are between 2.78 and 1.89. This implies that the surface heterogeneity is due to the adsorbate-adsorbent interactions as well

as the pore structure. The value of r in inorganic adsorbate(I_2) is greater than that of organic(CH_3I), i.e. its increase means that the heterogeneity of the carbon surface decreases in the inorganic adsorbate.

The DA isotherms of elemental iodine and methyl iodide in base carbon and TEDA impregnated carbons are shown in Figs. 5~8. Those figures show

good curve fits with experimental data as linear lines. The maximum adsorption capacity and the adsorption energy can be calculated from the interception and the slope of the DA isotherm line, respectively. The maximum methyl iodide adsorption amounts on base carbon and TEDA impregnated carbon by the DA equations are listed in Table 3.

The adsorbate molecules do not form a simple, regular monolayer on the surface. High-energy sites are covered first, and local multilayer coverage of these sites may even take place before total monolayer coverage of the surface occurs[20]. The heterogeneous surface model studied allows for the fact that adsorption is more likely to occur on high-en-

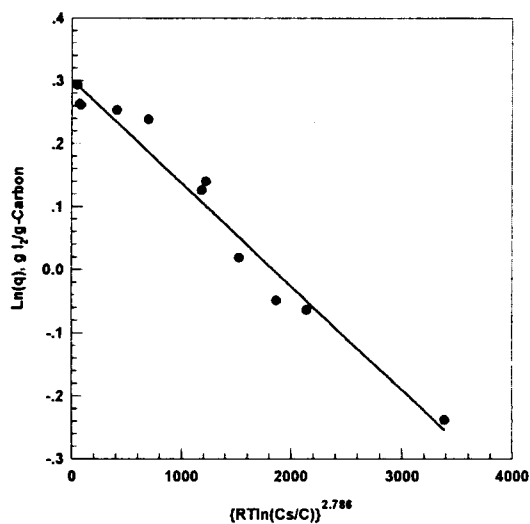


Fig. 5. DA Adsorption Isotherm of Elemental Iodine on Base Carbon at 30°C.

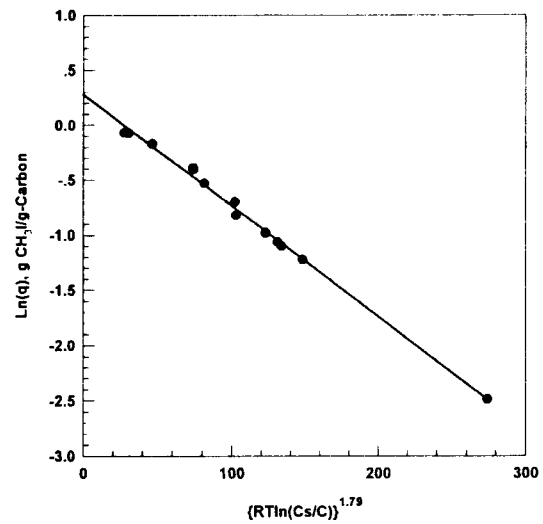


Fig. 7. DA Adsorption Isotherm of Methyl Iodide on 2% TEDA Impregnated Carbon at 30°C.

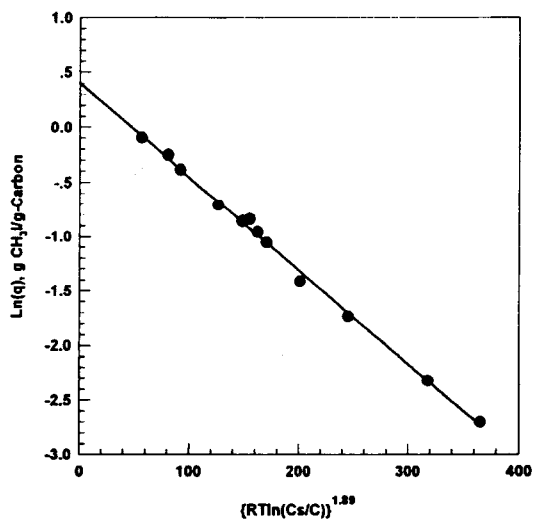


Fig. 6. DA Adsorption Isotherm of Methyl Iodide on Base Carbon at 30°C.

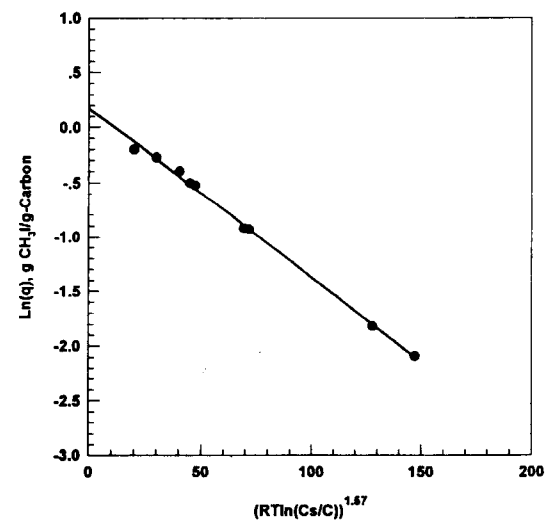


Fig. 8. Equilibrium Adsorption Isotherm of Methyl Iodide on 5% TEDA Impregnated Carbon at 30°C.

ergy than on low-energy sites and that, accordingly, a higher fraction of these sites is covered at any value of the coverage ratio[21].

Figs. 9~10 represent the adsorption energy distribution curves for each elemental iodine and methyl iodide on base carbon and TEDA impregnated carbon. The curve for elemental iodine on base carbon has almost a normal shape of a gaussian function, while those of methyl iodide have skewed adsorption energy distributions in shapes. The characteristic energy or the most probable adsorption energy, E , is 22.9 kJ/mol for the elemental iodine on base carbon, 12.4, 13.0, and 14.1 kJ/mol for the methyl iodide on the base carbon, 2% TEDA, and 5% TEDA impregnated carbon, respectively. The value of r of methyl iodide on the TEDA impregnated carbon decreases as the increase of TEDA impregnated content on the carbon, and the distribution curves become sharper in shape. These results mean that distribution curve becomes sharper as r increases, which implies a decrease in the energetic heterogeneity of the adsorbent surface. Therefore, the heterogeneity of carbon surface increases as the TEDA impregnated

content on the carbon increases.

6. Conclusions

For the purpose of radioiodine removal in the gaseous stream, the adsorption characteristics of elemental iodine and methyl iodide on a base and TEDA impregnated carbon were investigated. The major effect of impregnation is to trap strongly methyl iodide from effluent streams.

Adsorption isotherms were reviewed by various adsorption models and the DA equation gave the best fit for the adsorption of elemental iodine and methyl iodide on various carbons. Also, the DA equation was well suited to represent the physically adsorbed amount except for low adsorbate concentration in which the adsorption isotherm is linear. The adsorption energy distribution was calculated from the parameters of the DA equation based on the condensation approach. From the results, it was known that the iodine-carbon systems were highly heterogeneous due to the adsorbate-adsorbent interaction as well as

Table 3. Parameters of the DA Isotherm Equation and Deviation for Various Isotherms on Adsorption of Elemental Iodine and Methyl Iodide on Various Carbons.

System	Parameters of DA isotherm equation			Dev(%)			
	q_m (g/g carbon)	r	E (kJ/mol)	DA	Langmuir	Freundlich	Sips
I ₂ — Base carbon	1.35	2.78	22.9	2.59	6.1	5.86	2.72
CH ₃ I— Base carbon	1.50	1.89	12.4	3.02	17.7	8.22	3.60
CH ₃ I— 2% TEDA impregnated carbon	1.32	1.79	13.0	3.75	23.0	10.7	4.15
CH ₃ I— 5% TEDA impregnated carbon	1.19	1.57	14.1	2.7	20.4	6.94	3.55

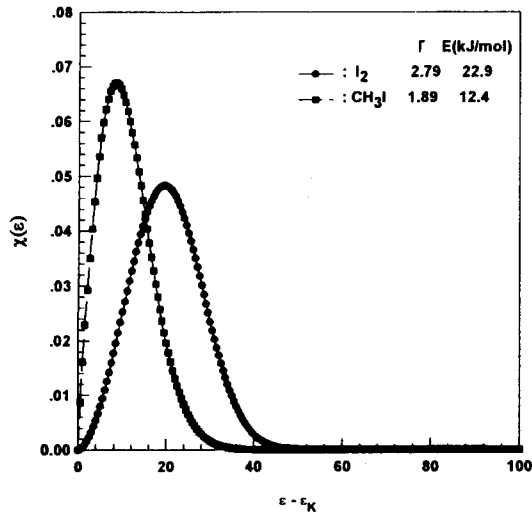


Fig. 9. Adsorption Energy Distribution Curves of Elemental Iodine and Methyl Iodide on Base Carbon at 30°C.

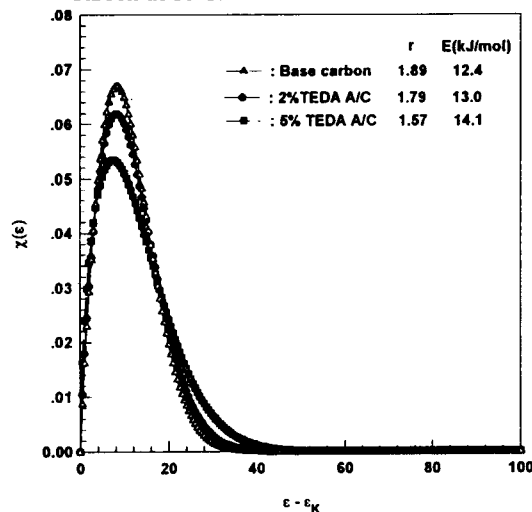


Fig. 10. Adsorption Energy Distribution Curves of Methyl Iodide on Various Carbons at 30°C.

the pore structure.

The surface heterogeneity increases as a content of TEDA impregnated increases. The adsorption nature of methyl iodide on carbon have shown more heterogeneous than that of elemental iodine.

Nomenclature

b Langmuir constant, m^3/mol

c concentration in the liquid phase, mol/m^3
 c_s saturated concentration in the liquid phase, mol/m^3
 dev (%) percent deviation defined in Eq. (10)
 E characteristic adsorption energy, J/mol
 K Freundlich coefficients in Eq. (2)
 N number of data points
 n exponent in Eq. (2) and (3)
 q amount adsorbed, mol/kg
 q_m amount adsorbed at the saturated concentration, mol/kg
 r parameter in the exponential energy distribution
 R gas constant, J/mol °K
 T temperature, °K

Greek Letters

ϵ energy of adsorption, J/mol
 ϵ_K critical adsorption energy, J/mol
 θ (p) total adsorption in terms of adsorbent surface coverage
 χ (ϵ) energy distribution function
 Ω interval of possible adsorption energy changes

References

1. D.O. Campbell, A.P. Malinauskas and W.R. Stratton, The chemical behavior of fission product iodine in light water reactor accidents, *Nuch. Tech.*, **53**, 111 (1981)
2. E.G.P. Cornelissens, G. Van Der Lugt and T. Van Der Plas, Adsorption of gaseous methyl iodide by active carbons, *Proc. IAEA/SM-89/43*, 647 (1989)
3. J.L. Kovach, J.J. Grimm and W.P. Freeman, TEDA vs. quinuclidine: Evaluation and comparison of two tertiary amine impregnants for methyl iodide removal from flow air stream, *Paper presented at the Proceedings of the 17th DOE*

- Nuclear Air Cleaning Conference*, 652 (1981)
4. S.H. Chang and W.J. Cho, Experimental and analytical study on the time-dependent removal efficiency of methyl iodide by an impregnated charcoal bed, *Nucl. Tech.*, **68**, 242 (1985)
 5. L.A. Jonas, V.R. Dietz and J.B. Romans, Desorption kinetics of methyl iodide from impregnated charcoal, *Nucl. Tech.*, **48**, 77 (1980)
 6. F.E. Dolian, and S. Hornats, Impregnated charcoal, *U.S. Report TDMR*, **767** (1943)
 7. D.A. Collins, L.R. Taylor and R. Taylor, Development of impregnated charcoals for trapping methyl iodide at high humidity, *Paper presented at the Proceedings of the 9th AEC Air Cleaning Conference, CONF-660904*, **1**, 159 (1966)
 8. L. Langmuir, The adsorption of gases on plane surfaces of glass, Mica, and Platinum, *J. Am. Chem. Soc.*, **40**, 1361 (1918)
 9. S.R. Olsen, and F. S. Watanabe, A method to determine a phosphorous adsorption maximum of soil as measured by the Langmuir isotherm, *Proc. Soil Sci. Soc. Amer.*, **21**, 144 (1957)
 10. C.H. Obihara and E.W. Russel, Specific adsorption of silicate and phosphate by soils, *J. Soil Sci.*, **23**, 105 (1972)
 11. M.K. John, Cadmium adsorption maxima of soils as measured by the Langmuir isotherm, *Canad. J. Soil Sci.*, **52**, 343 (1972)
 12. E.J. Ryden, J.R. McLaughlin, and J.K. Syers, Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel, *J. Soil Sci.*, **28**, 72 (1977)
 13. D. Gunary, A new adsorption isotherm for phosphate in soil, *J. Soil Sci.*, **21**, 72 (1970)
 14. D.M. Ruthven, *Principles of adsorption and adsorption processes*, John Wiley & Sons, New York (1984)
 15. R.T. Yang, *Gas separation by adsorption processes*, Butterworths, Boston (1986)
 16. W. Rudzinski and D.H. Everett, *Adsorption of gases on heterogeneous surfaces*, Academic Press, London (1992)
 17. H.F. Stoeckli, A. Lavanchy and F. Kraehenbuehl, *Adsorption at the gas-solid and liquid-solid interface*, (Rouquerol, J. and Sing, K.S.W. Eds.), p201, Elsevier Sci. Pub. Co., Amsterdam (1982)
 18. M. Jaroniec and R. Madey, *Physical adsorption on heterogeneous solids*, Elsevier Sci. Pub. Co., Amsterdam (1988)
 19. J. Oscik, *Adsorption*, Ellis Horwood Ltd., Chichester (1982)
 20. S.P. Boudreau and W.T. Cooper, Determination of surface polarity by heterogeneous gas-solid chromatography, *Anal. Chem.*, **59**, 353 (1987)
 21. J. Roles and G. Guiochon, Validity of the model used to relate the energy distribution and the adsorption isotherm, *J. Chromato.*, **591**, 267 (1992)