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KINETICS OF INTERCALATE DESORPTION FROM CARBON FIBERS INTERCALATED WITH BROMINE

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Abstract—This paper reports the kinetics of intercalate desorption from pitch-based carbon fibers intercalated by exposure to Br_2. The kinetics was studied by thermogravimetric analysis of brominated Thornel P-100 and P-X-7 carbon fibers of Amoco Corp., as P-X-7 was more graphitic than P-100. Comparison was made with previous kinetic data on highly oriented pyrolytic graphitic (HOPG) intercalated with bromine. The activation energies of desorption below 100°C were 9, 12, and 17 kcal/mol Br_2, respectively, for P-100, P-X-7, and HOPG. The values above 100°C were 8, 5, and 4 kcal/mol Br_2, respectively, for P-100, P-X-7, and HOPG. A high degree of order of the intercalate increases the activation energy below 100°C, whereas a high degree of graphitization decreases the activation energy above 100°C. Brominated P-100 retained a stable bromine concentration of 17.5 wt.% up to at least 200°C. This thermal stability is attributed to the relatively high activation energy of desorption of brominated P-100 above 100°C.

Key Words—Carbon fibers, intercalation, bromine, desorption, kinetics.

1. INTRODUCTION

Pitch-based carbon fibers (Thornel P-100 of Amoco) brominated by exposure to Br_2 have recently received much attention because the bromination decreased the electrical resistivity from 250 to 52 μΩ.cm and because this low resistivity was not changed over a period exceeding three years of exposure to the atmosphere[1]. Furthermore, the brominated P-100 fibers were stable in resistivity up to 200°C[2]. Bromine stood out as the intercalate that gave the best stability, compared to other intercalates such as IC1, $CuCl_2$ and $NiCl_2$[1]. The low electrical resistivity is attractive for electromagnetic interference shielding and for lightning protection of aircrafts.

Previous stability studies on brominated Thornel P-100 carbon fibers were made by monitoring the electrical resistivity[1,2]. This paper provides a complementary study by monitoring the bromine content, which is directly related to the chemical or environmental stability. Furthermore, this study provides information on the kinetics of bromine desorption from the fibers. From this information, we provide an explanation for the exceptional stability of brominated P-100 fibers.

Thornel P-100 carbon fibers brominated by exposure to Br_2 are intercalated, but the intercalate layers do not exhibit in-plane order at room temperature[3]. In contrast, highly oriented pyrolytic graphite (HOPG) and highly graphitic carbon fibers (e.g., Amoco's P-X-7 and du Pont's E-130) that have been brominated by exposure to Br_2 exhibit in-plane superlattice order at room temperature and up to 100°C, at which temperature in-plane melting occurs[4,5]. As the melting at 100°C is known to affect the kinetics of bromine desorption from HOPG[6], it is interesting to investigate its effect in the case of carbon fibers.

The thermal stability of the resistivity increased with decreasing degree of graphitization, as shown by comparing the behavior of Amoco P-75, P-100, and P-120 carbon fibers (listed in order of increasing degree of graphitization)[2]. Therefore, this paper also investigates how the structural difference between P-100 and more highly graphitic fibers affects the desorption kinetics.

2. EXPERIMENTAL

2.1 *Sample preparation*

Two types of pitch-based carbon fibers were used. They were Thornel P-100 and P-X-7, both kindly provided by Amoco Corp. Although both are among the most graphitic types of carbon fibers, P-X-7 is even more graphitic than P-100. The P-100 fibers are commercially available, but the P-X-7 fibers are experimentally available.

Bromination of either type of fibers was carried out by exposure of the fibers (without resin sizing) to bromine vapor in air at room temperature for at least six days.

2.2 *Experimental method*

The bromine content in the fibers was obtained by measuring the weight of the fibers before and after bromination. In order to study the bromine desorption kinetics after bromination, the weight of the fibers was measured in air as a function of time and temperature up to 200°C. Such temperatures are too low for weight loss due to oxidation of carbon fibers, as independently shown by mass spectro-

metric observation of the evolved CO_2 as a function of temperature[7].

The thermogravimetric measurement was performed by using a Perkin-Elmer electronic microbalance (Autobalance Model AD-2Z), which has a maximum sensitivity of 0.1 μg. The sample was placed on a platinum pan suspended by a platinum hangwire. A quartz tubing (25.4 mm inside diameter) enclosed the hangwire and the sample pan. During measurement the tube was slowly purged with nitrogen at a rate of approximately 15 cm^3/min. A low mass furnace surrounded the sample pan and was controlled by a Theall Engineering Model TP-2000 temperature programmer capable of either isothermal or scanning temperature control. The sample temperature was measured by placing a chromel-alumel thermocouple immediately below (within 2 mm of) the sample pan.

2.3 *Experimental results*

2.3.1 *Scanning thermogravimetric analysis (TGA).* Figures 1 and 2 show the thermogravimetric data of brominated P-100 and brominated P-X-7, respectively. The data for brominated P-100 were obtained after five days of room temperature desorption; the data for brominated P-X-7 were obtained after three days of room temperature desorption. The samples were heated at a rate of 10°C/min and the weight of each sample was about 20 mg. Both sets of data show an onset of significant bromine desorption at 100°C, the temperature for in-plane melting of graphite intercalated with bromine[8]. However, a clearer onset was observed for brominated P-X-7 than brominated P-100.

2.3.2 *Isothermal desorption.* Isothermal desorption was studied on brominated P-100 and brominated P-X-7. The weight of each sample was about 20 mg.

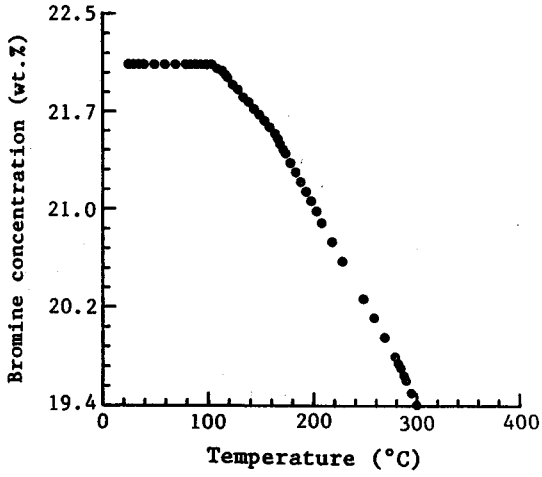


Fig. 2. Bromine concentration (% by weight of parent fibers) versus temperature during heating for brominated P-X-7 fibers.

2.3.2.1 *Brominated P-100.* Figure 3 shows the bromine concentration as a function of time for brominated P-100 desorbed at 60, 70, 80, and 90°C. During the early part of the desorption process, the desorption rate increased as the temperature increased. Complete desorption did not occur because a significant portion of the original bromine (equivalent to 20 wt.% of the parent fibers) was retained by the fibers even after a long desorption time. This stable bromine concentration of 20 wt.% was attained at all temperatures below 100°C (i.e., 60, 70, 80, and 90°C), although the time needed to attain stability increased with decreasing temperature.

In analyzing the data, the stable bromine concentration was subtracted from the total bromine concentration to yield the "desorbable" bromine con-

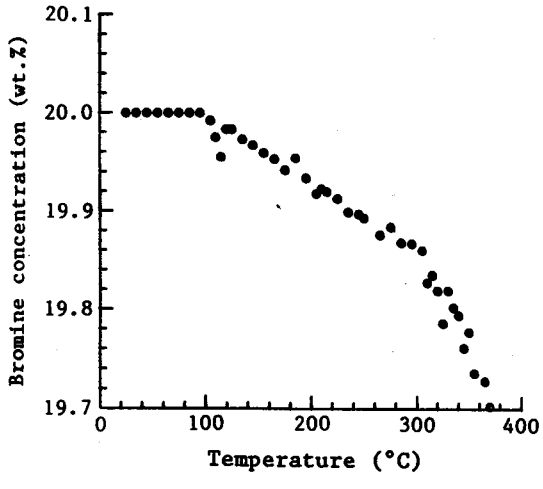


Fig. 1. Bromine concentration (% by weight of parent fibers) versus temperature during heating for brominated P-100 fibers.

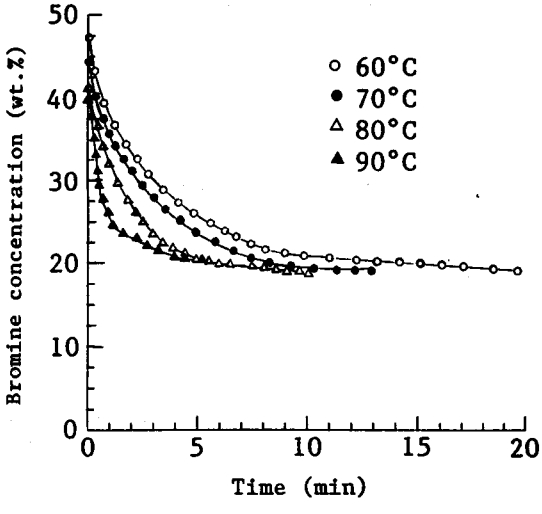


Fig. 3. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures below 100°C for brominated P-100 fibers.

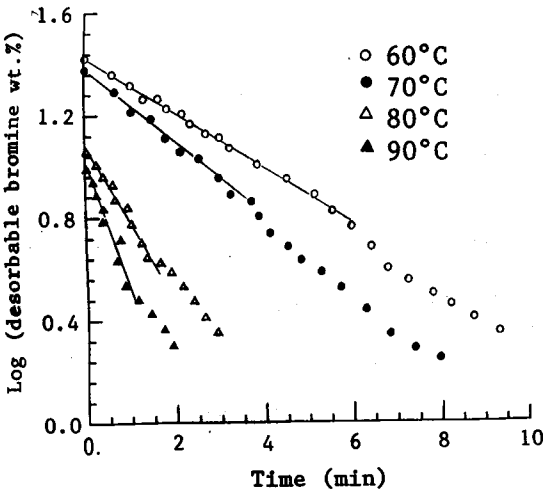


Fig. 4. Logarithm of the desorbable bromine concentration versus time at different constant temperatures below 100°C for brominated P-100 fibers.

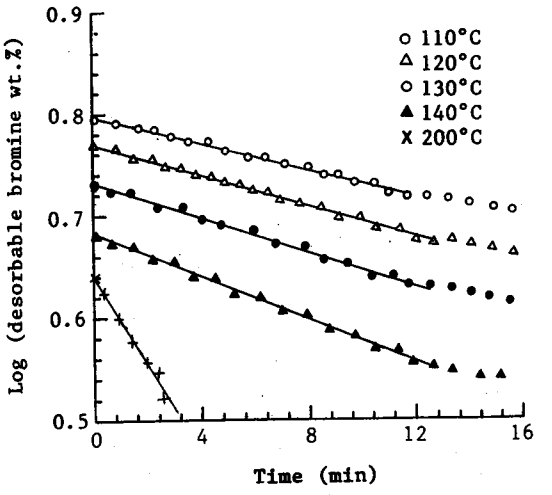


Fig. 6. Logarithm of the desorbable bromine concentration versus time at different constant temperatures above 100°C for brominated P-100 fibers.

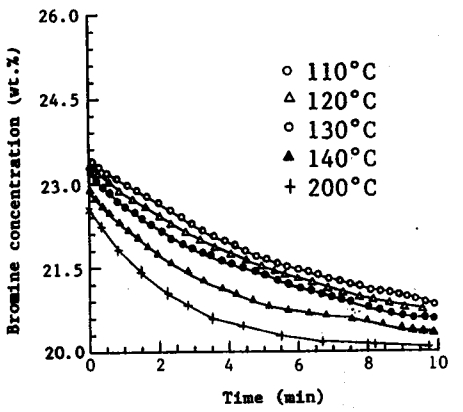
centration C^*. In other words,

$$C^* = \frac{M_{Br} - M_S}{M_C}, \qquad (1)$$

where M_{Br} is the mass of bromine at a given time, M_S is the mass of bromine at the stable bromine concentration and M_C is the mass of the parent fibers. Figure 4 shows the logarithm of the desorbable bromine concentration, log (C^*), as a function of time.

Desorption curves for desorption at temperatures above 100°C are shown in Fig. 5(a) for times up to 10 min and in Fig. 5(b) for times up to 4 h. Because of the high desorption rate at 100°C (see section 2.3.1), it was impossible to maintain a high bromine concentration above 100°C. As a result, measurements above 100°C could only be performed on relatively dilute samples (less than 25 wt.% bromine). The temperatures chosen for isothermal measurements were 110, 120, 130, 140, and 200°C. The desorption rate increased as the temperature increased, as in the case of desorption below 100°C. As shown in Fig. 5(b), desorption at these temperatures led to a stable bromine concentration of 17.5 wt.%. The desorbable bromine concentration was obtained using eqn (1) with this value of the stable bromine concentration, and its logarithm was plotted against time, as shown in Fig. 6.

2.3.2.2 *Brominated P-X-7.* Figure 7 shows the bromine concentration as a function of time for brominated P-X-7 desorbed at 60, 70, 80, and 90°C. At these temperatures below 100°C, a bromine concentration of 22 wt.% remained in the fibers even



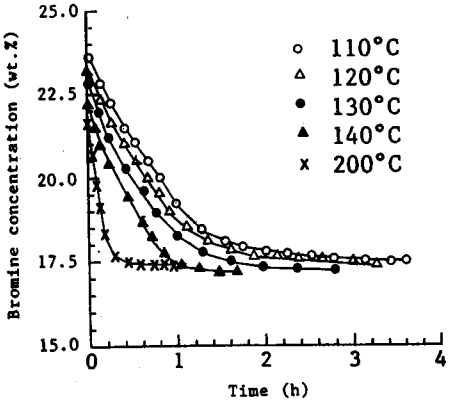


Fig. 5. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures above 100°C for brominated P-100 fibers. (a) up to 10 min; (b) up to 4 h.

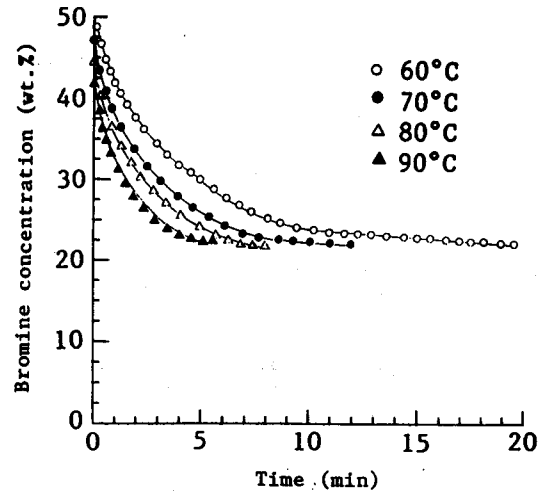


Fig. 7. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures below 100°C for brominated P-X-7 fibers.

after very long desorption times. This amount was thus subtracted from the total amount of bromine to yield the "desorbable" portion of the bromine, as shown in Fig. 8. Comparison of brominated P-X-7 (Figs. 7 and 8) with brominated P-100 (Figs. 3 and 4) shows that the desorption rate of brominated P-100 at temperatures below 100°C was faster than that of brominated P-X-7.

Figure 9 shows the bromine concentration as a function of time for brominated P-X-7 desorbed at 110, 130, and 140°C. After long times of desorption, the fibers became stable at 17.5 wt.% bromine, as shown in Fig. 9(b). The desorbable bromine concentration is shown versus time in Fig. 10. Comparison of Figs. 9 and 5 shows that the desorption rate of brominated P-X-7 at temperatures above 100°C was faster than that of brominated P-100.

2.3.3 *Analysis.* The desorption process is probably diffusion controlled, as suggested by the kinetics of desorption from brominated HOPG[6] and the kinetics of bromination of HOPG[9]. The desorbable bromine concentration remaining in the fibers at time t is then approximately proportional to $\exp(-kt)$, where k is the rate constant for the desorption process[10]. Hence, the rate constant k can be determined from the initial slope of the plot of the logarithm of the desorbable bromine concentration versus time. That is,

$$-k = \frac{d(\ln C^*)}{dt}, \tag{2}$$

For a diffusion process, the rate constant k increases with temperature in the form

$$k = k_o \exp\left(-\frac{E_D}{k_B T}\right), \tag{3}$$

where k_o is a constant of proportionality, E_D is the activation energy of desorption, and k_B is the Boltzmann's constant and T is the temperature in K. A plot of $\log k$ verus $1/T$ yields a straight line, the slope of which is $-0.434\ E_D/k_B$.

The desorption process at high bromine concentrations (above 26 wt.%) could be studied only at temperatures below 100°C, because of the more severe desorption above 100°C.

Arrhenius plots that give the activation energy E_D are shown in Fig. 11 for temperatures below 100°C and in Fig. 12 for temperatures above 100°C. Table 1 lists the values of E_D obtained.

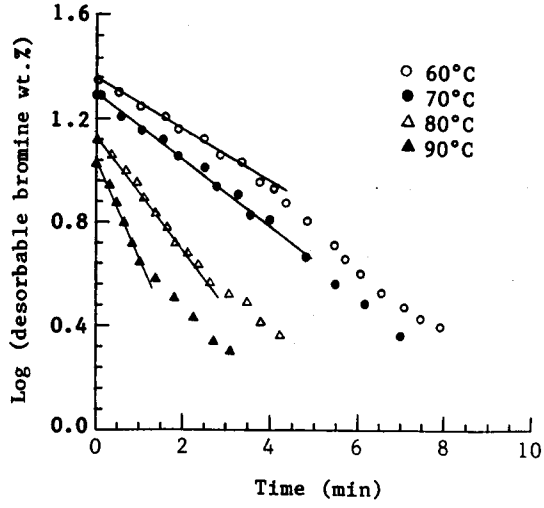


Fig. 8. Logarithm of the desorbable bromine concentration versus time at different constant temperatures below 100°C for brominated P-X-7 fibers.

3. CONCLUSION AND DISCUSSION

The stable bromine concentration is a technologically important quantity because practical use of brominated fibers involves the stable form of the fibers. Table 2 lists the stable bromine concentrations for P-100 and P-X-7 fibers. The stable bromine concentration below 100°C is higher for P-X-7 than P-100, but is the same for the two types of fibers above 100°C.

The desorption rate of brominated P-100 is faster than that of brominated P-X-7 at temperatures below 100°C, but is slower than that of brominated P-X-7 at temperatures above 100°C.

The activation energy of desorption from brominated P-100 is lower than that of brominated P-X-7 at temperatures below 100°C, but is higher than that of brominated P-X-7 above 100°C.

The values of the activation energy of desorption are similar for brominated P-100 below 100°C and above 100°C, whereas the values are quite different

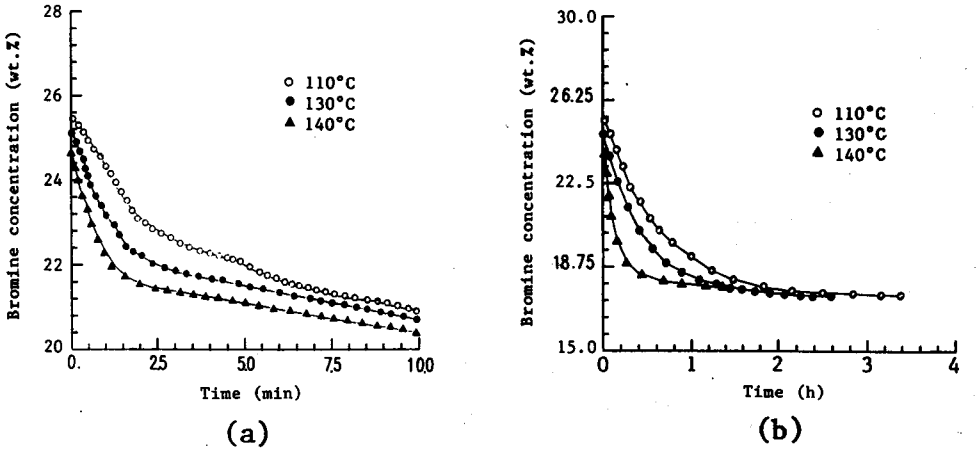


Fig. 9. Bromine concentration (% by weight of parent fibers) versus time at different constant temperatures above 100°C for brominated P-X-7 fibers. (a) up to 10 min; (b) up to 4 h.

for brominated P-X-7 below 100°C and above 100°C. A substantial difference in the activation energy of desorption had been reported for brominated HOPG below 100°C and above 100°C[6], as shown in Table 1, which indicates that the activation energy of desorption increases with increasing degree of graphitization below 100°C, but decreases with increasing degree of graphitization above 100°C. The increase of the activation energy with increasing degree of graphitization below 100°C is due to the fact that the degree of intercalate order increases with increasing degree of graphitization. In this context, it should be noted that in-plane intercalate order is absent in brominated P-100 below 100°C, but is present in brominated P-X-7 and brominated HOPG below 100°C. It is further expected that staging is clearer in brominated HOPG than brominated P-X-7. Above 100°C, the intercalate is not ordered for P-100 and P-X-7, as well as HOPG, and an increase in the degree of graphitization decreased the concentration of defects, which hinder desorption. As a result, the activation energy of desorption above 100°C decreased with increasing degree of graphitization. This is probably the basis of the exceptionally good stability reported by others (based on electrical resistivity measurements) for brominated P-100 up to 200°C[2]. Consistent with the resistivity results of ref. 2, this work found through weight measurement that brominated P-100 retains a stable bromine concentration of 17.5 wt.% up to at least 200°C.

A high activation energy of desorption above 100°C is particularly relevant to environmental stability as it pertains to the stability of the more tightly held bromine, which remains after desorption below 100°C is complete. The exceptionally high stability of brominated P-100 is therefore related to the rela-,

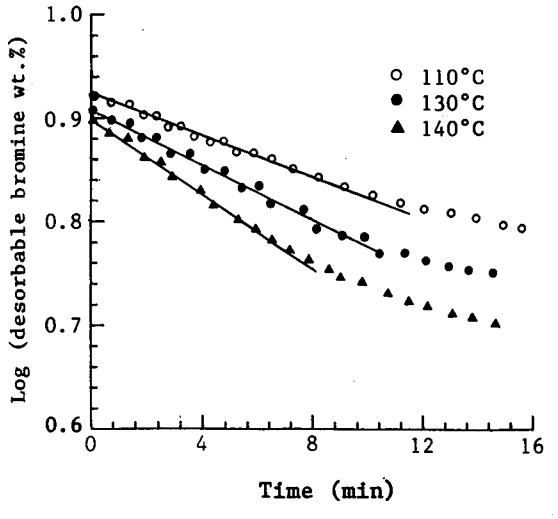


Fig. 10. Logarithm of the desorbable bromine concentration versus time at different constant temperatures above 100°C for brominated P-X-7 fibers.

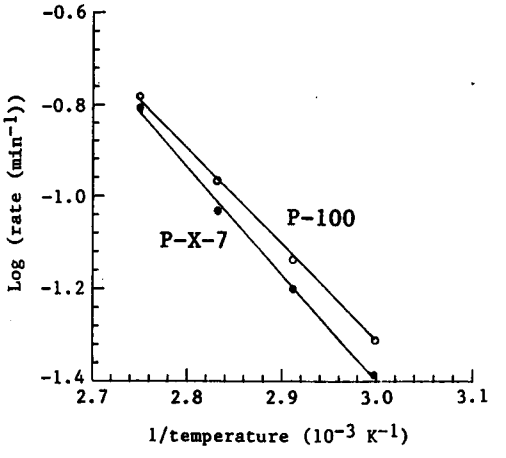


Fig. 11. Arrhenius plot of the desorption rate versus 1/temperature for temperatures below 100°C for brominated P-100 fibers (○) and brominated P-X-7 fibers (●).

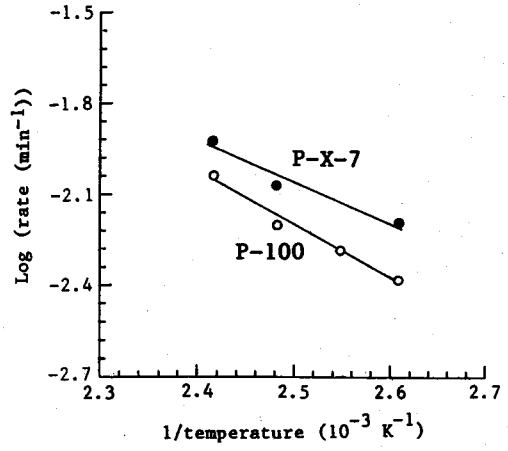


Fig. 12. Arrhenius plot of the desorption rate versus 1/temperature for temperatures above 100°C for brominated P-100 fibers (○) and brominated P-X-7 fibers (●).

tively high activation energy of desorption of brominated P-100 above 100°C. That the activation energy above 100°C increases in the order HOPG, P-X-7, and P-100 is consistent with the report[2] that the thermal stability of the resistivity increases with decreasing degree of graphitization.

The onset of more severe desorption occurs at 100°C during temperature scanning for both brominated P-100 and brominated P-X-7 (Figs. 1 and 2), but the onset is clearer for brominated P-X-7 than for brominated P-100. This is due to the melting of the intercalate in brominated P-X-7 at 100°C and the fact that the intercalate in brominated P-100 is already molten at room temperature[2]. Though less clear, there is still an onset at 100°C for brominated P-100. This is because the chemical state of the bromine intercalate is basically similar in P-100 and P-X-7, as indicated by the intercalate Raman peak around 240 cm^{-1}.

Table 1. Activated energy of desorption from brominated carbon fibers

	Activation energy (kcal/mol Br_2)	
	Below 100°C	Above 100°C
P-100	9	8
P-X-7	12	5
HOPG	17*	4*

*From ref. 6.

Table 2. Stable bromine concentration in brominated carbon fibers

	Stable bromine concentration (wt.%)	
	Below 100°C	Above 100°C
P-100	20	17.5
P-X-7	22	17.5

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COMPOSITE SORBENTS BY CHEMICAL VAPOR DEPOSITION ON ACTIVATED CARBON

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Abstract—Composite sorbents were prepared by depositing approximately monolayers of Br_2 or ICl on activated carbon. Methane adsorption remained equal on these sorbents whereas the adsorption of N_2 was reduced. The selectivity ratio of CH_4/N_2 was increased to approximately 4 on the composite sorbents, making them promising candidates for CH_4/N_2 separation. The reduction of adsorption seems to be caused by the occupation of the sites by the quadrupolar Br_2 or ICl molecules; these sites would otherwise adsorb N_2, which is also quadrupolar.

Key Words—Composite sorbents, methane/nitrogen separation, CVD on carbon.

1. INTRODUCTION

The separation of N_2 and CH_4 is a costly step in natural gas processing. Much of the natural gas resources is not usable presently because the N_2 content is too high (well above 10% by vol). The minimum requirement for the CH_4 content is 90% for commercial use. Moreover, the N_2 content increases with time after the reservoir is in service[1]. The only commercial means for N_2/CH_4 separation at the present time is by costly cryogenic separation[1]. Adsorption processes have not been applied to this separation because there are no known sorbents that possess the required selectivity.

In this study, composite activated carbon sorbents are prepared by depositing nearly monolayer amounts of Br_2 and ICl on the carbon surface. Br_2 and ICl both possess quadrupole moments, similar to N_2, whereas CH_4 does not. HNO_3 treated carbon is also used as a reference sorbent because the surface oxidation by HNO_3 creates highly polar surfaces on carbon[2].

2. EXPERIMENTAL

The activated carbon used in this study was BPL Calgon carbon. The chemicals were of ACS grades supplied by Alfa Products (Morton Thiokol). Impregnations were performed on 12 × 30 mesh activated carbon. The Br_2 impregnation was carried out at room temperature. The activated carbon was placed inside a closed glass chamber with a Br_2 reservoir and the bromine vapor was allowed to react with the carbon for seven days. The vapor pressure of the Br_2 at room temperature was estimated to be 22 kPa (165 torr). After seven days, the carbon was removed from the closed glass chamber and allowed to equilibrate with air to desorb the excess bromine vapor. Frequent weighings were performed to determine the equilibration time. About five days were required to achieve no detectable weight changes. By weighing the BPL activated carbon before and after the impregnation, the percent loading of Br_2 was determined. By expressing the percent loading relative to the untreated carbon, a loading of 40 wt % was obtained, which corresponded to 22% of the pore volume occupied by Br_2 (assuming Br_2 density = 3.1 g/cm³). The method of impregnation with the vapor of nitric acid is identical to that described for the case of bromine except that red fuming HNO_3 was used instead of Br_2. The carbon was exposed to HNO_3 vapor at room temperature. A loading of 10 wt % HNO_3 was obtained for the case of nitric acid impregnation. The ICl impregnation was carried out at 90°C. The activated carbon was placed in a glass vial, and the vial (open) was placed at the bottom of a vertical tube containing about 5.0 ml of liquid ICl, which did not reach the top of the vial. The vertical tube was then sealed and subsequently heated to 90°C for three days. Extreme care was taken so as to avoid contacting the ICl (liquid) with the activated carbon, as vapor-phase impregnation was intended. After three days, the sealed tube was allowed to cool for 24 h before the glass tube was broken. The sample was allowed to desorb at room temperature until no weight loss. Again by weighing the activated carbon before and after the vapor phase impregnation, the loading was 40 wt %, which corresponded to 21% pore volume occupied by ICl assuming the density of deposited ICl = 3.2 g/cm³. To minimize the adsorption of moisture, all samples were weighed in sealed weighing vials, which were sealed promptly after heating at 100°C.

Adsorption isotherms were measured gravimetrically, using a Mettler TA 2000C thermoanalyzer for pressures below 1 atm. For isotherms at above 1 atm pressure, a static volumetric system was used. Prior to the measurements, the sorbents were regenerated overnight at 100°C. This regeneration

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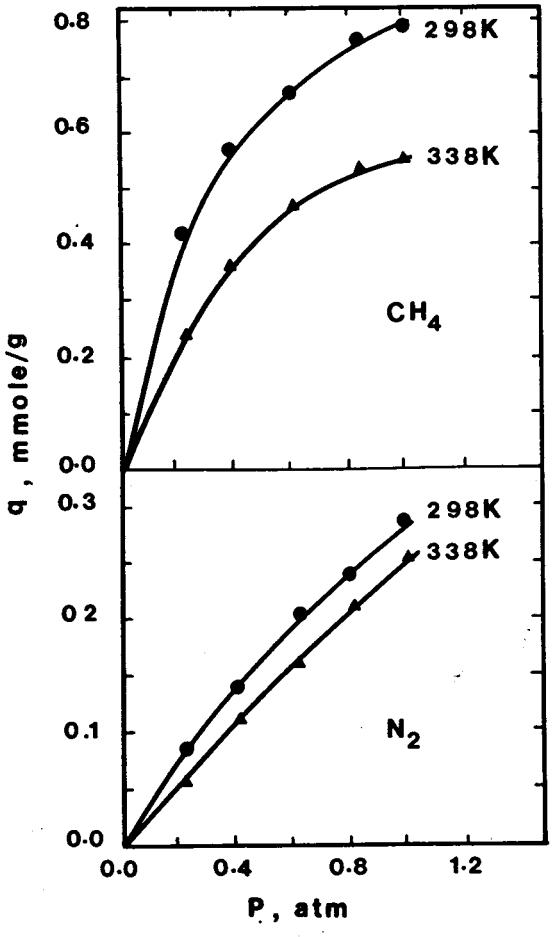

Fig. 1. Equilibrium adsorption (q) on BPL activated carbon.

condition was established because it enabled thorough desorption of the adsorbates, and at the same time the CVD deposition was not affected as evidenced by the return to the same weights. The isosteric heats of adsorption were estimated from isotherms at two temperatures. A Quantasorb surface area analyzer (Quantachrome Corporation) was used for BET surface area determination. Gases were supplied by Cryogenic Supply (Union Carbide Corporation), with a minimum purity of 99.9%. The water vapor was obtained by passing a helium carrier through a water saturator maintained at 25°C.

3. RESULTS AND DISCUSSION

The equilibrium adsorption of gas mixtures may be predicted based on single-gas isotherms. Predictive theories and models have been reviewed and discussed elsewhere[3]. A good indication for the selectivity of a sorbent may be obtained from the single-gas isotherms.

3.1 *Sorbent characterization*

The BET surface areas for the sorbents before and after chemical vapor deposition were: activated carbon (800 m^2/g), HNO_3 treated carbon (710 m^2/g), Br_2 deposited carbon (720 m^2/g), and IC1 deposited carbon (510 m^2/g). These surface areas were based on the unit weight of the composite sorbents.

The HNO_3 treated carbon resulted in a 10% weight gain, which was due mainly to the formation of surface oxides. The weight gains associated with Br_2 and IC1 deposition were both 40%. The pore size distribution data of BPL carbon showed that the pores were mainly micropores with a size range of 10–20Å, and only a small fraction of pores were larger than 20Å. Consequently, multilayer deposition/adsorption of Br_2 and IC1 (e.g. more than two layers) would have totally blocked the micropores, and the N_2 BET surface area would have sharply decreased. However, the N_2 BET surface area of the carbon (800 m^2/g) was decreased only slightly for Br_2 deposited (to 720 m^2/g) carbon, and the IC1 deposited carbon maintained a high surface area of 510 m^2/g. These facts indicated that most of the micropores were still accessible to N_2 (in BET surface area measurement) and that the deposited Br_2 and IC1 were not multilayer. The weight gain data correspond to an area of 53 $Å^2$/molecule of Br_2 and 54 $Å^2$/molecule of IC1, calculated based on the N_2 BET

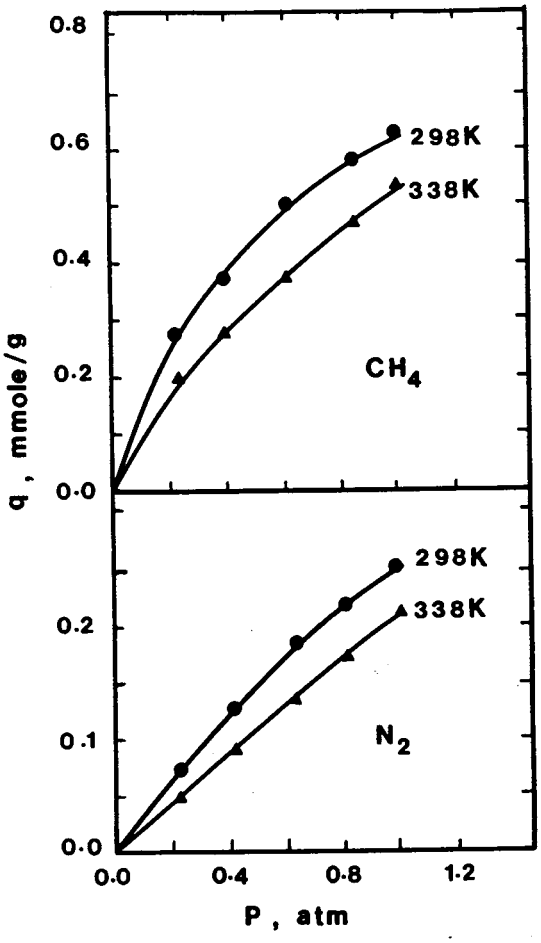

Fig. 2. Equilibrium adsorption (q) on HNO_3 treated activated carbon.

surface area of 800 m^2/g. These were reasonable values for monolayer or submonolayer deposition.

3.2 *Equilibrium isotherms and CH_4/N_2 selectivities*

The single-gas CH_4 and N_2 isotherms at two temperatures (298 and 338 K) for the four sorbents are shown in Figs. 1–4. The water vapor isotherms are shown in Fig. 5.

The discussion will be focused on the Br_2 and ICl deposited carbon because the HNO_3 treated carbon is quite well understood (see, for example, [2]). Comparing Fig. 1 (untreated carbon) and Fig. 3 (Br_2 deposited on carbon), the amount of CH_4 adsorption was approximately equal (based on BET surface areas of the respective sorbents), while the N_2 adsorption was substantially reduced on the Br_2 deposited carbon. The same conclusion was reached by comparing Figs. 1 and 4 (ICl deposited carbon). An explanation of these results is given as follows. Methane does not possess dipole or quadrupole moments, and the adsorption of CH_4 on all sorbents is due to van der Waals forces. Hence, equal adsorption on all three sorbents was expected. Nitrogen, on the other hand, possesses a quadrupole moment, and its adsorption is influenced by the polarity of

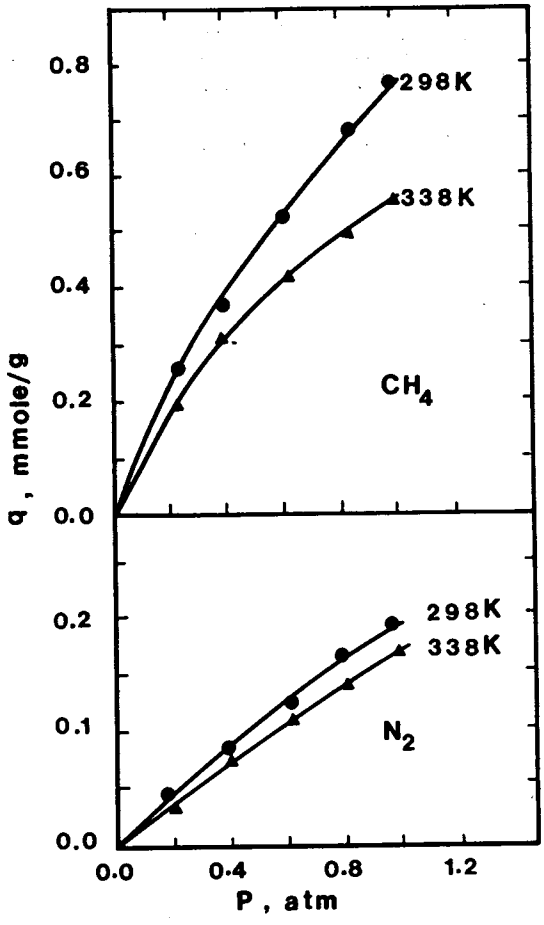

Fig. 3. Equilibrium adsorption (q) on Br_2 deposited (approximately monolayer) on activated carbon.

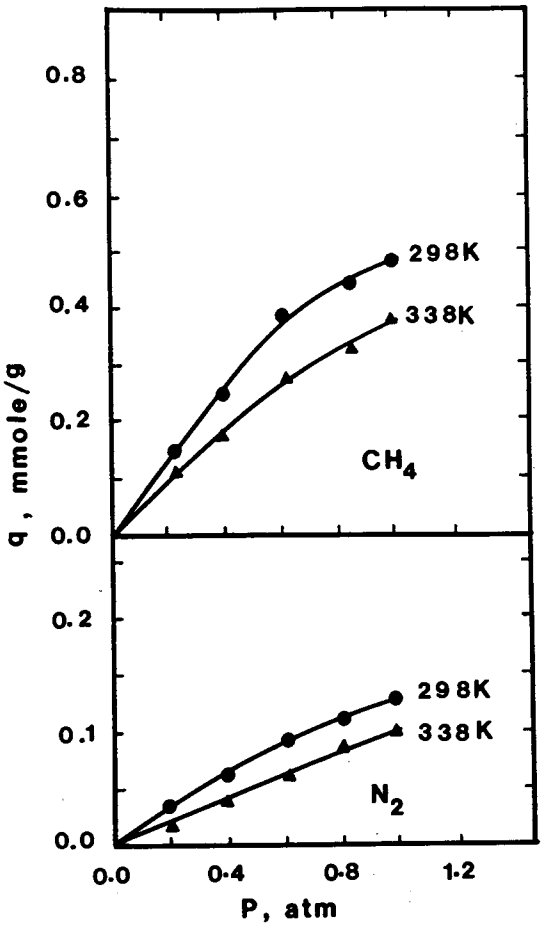

Fig. 4. Equilibrium adsorption (q) in ICl deposited (approx. monolayer) on activated carbon.

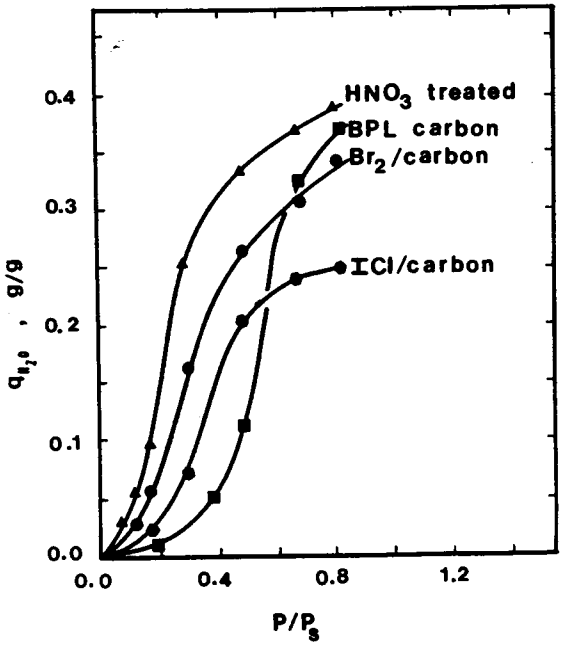

Fig. 5. Adsorption of water vapor at 298 K.

Table 1. Approximate mean heats of adsorption for CH_4 (<0.06 monolayer coverage) and N_2 (<0.04 monolayer coverage)

Adsorbent	CH_4, kcal/mole	N_2, kcal/mole
Carbon	3.3	1.3
HNO_3 treated	2.6	1.6
Br_2/carbon	1.7	0.8
ICl/carbon	2.4	2.2

the surface. Both Br_2 and ICl possess a quadrupole moment. The reduced N_2 adsorption on the Br_2 and ICl deposited carbon indicated that the sites favorable for N_2 were occupied by Br_2 and ICl, because they are all quadrupolar.

The water vapor isotherms (Fig. 5) showed that the adsorption was enhanced in the low concentration range for all three treated sorbents, with HNO_3 being the strongest. This result may be attributed to the increased surface polarity on all three samples. With Br_2 or ICl, however, the water vapor capacity at the high relative pressure range was decreased. This was due to the reduction of the total pore volume (as in the pore-filling theory) as a result of Br_2 or ICl deposition. The pore volume was not significantly reduced by HNO_3 oxidation.

The isosteric heats of adsorption calculated from Figs. 1–4 are given in Table 1. These values indicated that the bond strengths between CH_4 and the surfaces were higher than those with N_2. However, the equilibrium amount adsorbed is determined by both enthalpy and entropy of adsorption. Since the enthalpies of adsorption of CH_4 (Table 1) were reduced for both Br_2 and ICl deposited carbon, it appeared that the entropies of adsorption of CH_4 were increased on both samples. This result indicated that a more favorable geometric fit was possible between CH_4 and the composite carbons. For N_2 adsorption, a similar behavior was observed for the Br_2 deposited carbon, whereas the behavior on the ICl deposited carbon was different.

The CH_4/N_2 selectivities for the four sorbents are shown in Fig. 6. The selectivity was significantly improved by Br_2 or ICl deposition, due to the suppression of N_2 adsorption. The enhanced selectivity (to nearly 4) is promising indeed for the separation of CH_4 and N_2, as a selectivity for N_2/O_2 on zeolite of nearly 3 is adequate for commercial air separation[3]. The CH_4/N_2 selectivity for the Br_2/carbon at 2.02 atm was 3.54, compared to 2.42 for the untreated BPL carbon. Since a selectivity of approximately 3 appears to be an economic threshold for commercial bulk gas separation application, the composite sorbents are promising candidates for CH_4/N_2 separation.

The adsorption of Br_2 on activated carbon both from aqueous solution[4] and on carbons degassed

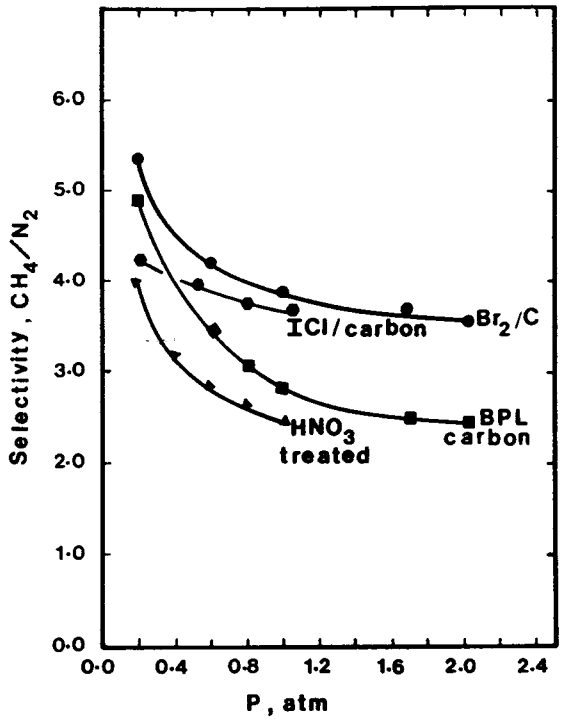

Fig. 6. Adsorption selectivity ratio of CH_4/N_2 at 298 K.

at various temperatures[5] has been studied extensively by Puri *et al.* The adsorption of Br_2 from aqueous solution reduced the pore volumes of carbons by approximately 25%[4], which is close to our value of 22% (see Section 2). The adsorbed Br_2 could not be degassed at temperatures as high as 1,200°C, and it was suggested that bromine was not molecularly adsorbed. Furthermore, the interaction between the halogens and the activated carbon has been reported to cause a large increase in the electrical conductivity, which was explained by the polarization of the halogen molecules in the adsorbed layer[6]. This phenomenon may play a role in causing the effects reported in this article.

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