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SHORT COMMUNICATION

LANGMUIR PARAMETERS FOR ADSORPTION OF TWO HALOGENATED CHEMICALS ON AN ACTIVATED CARBON PELLET

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Abstract – 1,1,2-trichloro-2,2,1-trifluoroethane is considered to be the prime contributor to stratospheric ozone depletion. Besides, dischloromethane is toxic. As a result, the use of activated carbon to adsorb these chemicals has been received a great attention. In this study, adsorption isotherms of 1,1,2-trichloro-2,2,1-trifluoroethane and dichloromethane on an activated carbon pellet were measured. The equilibria of these chemicals on activated carbon pellet were well expressed by Langmuir equation, and the equilibrium constants were expressed as function of temperature between 298 K and 393 K. Isosteric heats of adsorption were also evaluated from the experimental data.

Key words: Halogenated Chemicals, Adsorption, Langmuir Parameters

INTRODUCTION

The halogenated carbons such as dichloromethane and 1,1,2-trichloro-2,2,1-trifluoroethane have been used as solvents to clean delicate instruments, metal parts and surfaces. Furthermore, these chemicals are widely used as an extraction solvent in food and pharmaceutical processing were its high volatilities are desirable [Wolf et al., 1991]. In spite of its usefulness, the emissions of 1,1,2-trichloro-2,2,1-trifluoroethane are forbidden by Montreal Protocol [Andersen, 1991; Cicerone et al., 1974; Molina and Rowland, 1974].

On the other hand, American Conference of Governmental Industrial Hygienists (ACGIH) reported that the Threshold Limit Value (TLV) for dichloromethane is 50 ppmv as the 8 hour Time-Weighted Average (TWA). The repeated contact with dichloromethane may result in dermatitis, headache, giddiness, tingling in the limbs [Allen, 1989]. The ACGIH has classified it as a suspected human carcinogen (Group A2). Because of the toxicity of dichloromethane, it has been listed as one of the hazardous air pollutants in the US Clean Air Act Amendments (CAAA) of 1990.

One way to control the emission of these chemicals is the carbon adsorption technology [Kuo and Hines, 1988; Cho, 1994; Kodama et al., 1992; Tsai and Chang, 1994]. This technology is a very common one, because it offers some advantages. The advantages include the possibility of the recovery of raw materials for recycling and the high removal efficiency at low concentration. Besides, this technology requires the low energy costs. The adsorption equilibria and heat of adsorption are the important factors for the design of adsorption facilities.

In this study, the adsorption equilibria of two chemicals on activated carbon pellet were investigated. From the experimental data, isosteric heats of adsorption are evaluated, respectively.

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EXPERIMENT

An activated carbon pellet supplied by Norit (type; B4) was employed as an adsorbent. This activated carbon pellet had the dual pore structures and Table 1 show the properties of this adsorbent. The BET surface area for this adsorbent was measured by the nitrogen adsorption at 77 K with automatic sorption analyzer (Quantachrome: Autosorb-1). Its value was estimated to be 826 m^2/g. Dichloromethane and 1,1,2-trichloro-2,2,1-trifluoroethane were employed as two adsorbates and its' purities were 99.9%.

A conventional isotherm equipment was used for generation of equilibrium data (Micrometrics: Accusorb-2100E). this equipment employs a volumetric method for the measurement of adsorption equilibria. Before the experiments of adsorption, the adsorbent was regenerated in evacuated system at 473 K and regeneration time typically required about 15 hours. The weight of the sample was measured within 10 g accuracy and the dead volume was measured using helium gas. Oil diffusion pump and mechanical vacuum pump in combination provide vacuum down to 10^{-5} mmHg. Adsorption isotherms were obtained by the successive increments of the measured volumes to the ad-

Table 1. Physical properties of the activated carbon pellet

	Activated carbon pellet
Supplier (model no.)	Norit(B4)
Pellet diameter	0.37
Pellet length (cm)	0.65
BET surface area* (m^2/g)	826
Pore distribution**	
Micropores (<1 nm)	45.16%
Transition pores (1-100 nm)	9.68%
Macropores (>100 nm)	45.16%
Pore volume*** (cm^3/g)	0.49

*from nitrogen adsorption at 77 K (0.162 nm^2/molecule).
** from manufacturer.
*** from D-R plot.

sorbent. After each increment of gas admitted, time was allowed for the attainment of equilibrium and the system pressure was then noted.

A correction of the known volume of gas admitted for the amount unadsorbed in the dead space yielded a point on the adsorption isotherm. Equilibrium data for the caron pellet were obtained by similar procedures varying the temperatures.

RESULTS AND DISCUSSION

Adsorption equilibria of volatile organic chemicals (VOCs) on commercial adsorbents have been correlated by means of the Langmuir correlation in several cases [Kodama et al., 1992; Tsai and Chang, 1994]. It is convenient that adsorption equilibria are represented by this correlation, in order to design adsorption facilities. The experimental data obtained from this study were found to be described the Langmuir correlation:

$$W=\frac{A \cdot C}{1+B \cdot C} \quad (1)$$

The parameters A and B are functions of temperature. This loading equation is used not only or calculation of the loading, but also for the calculation of the isosteric heats of adsorption.

The Langmuir parameters obtained from experimental data for two adsorbates are listed in Table 2.

Table 2. The Langmuir parameters for two adsorbates

Adsorbates	Temp., K	A	B	Dev.
Dichloro-methane	323	0.00064	0.00018	7.24
	373	0.00037	0.00010	5.32
	396	0.00013	0.00004	6.72
	423	0.00006	0.00002	6.16
	473	0.00003	0.00001	5.20
1,1,2-trichloro-2,2,1-trifluoro ethane	298	0.00137	0.00219	6.31
	313	0.00095	0.00174	8.28
	343	0.00055	0.00127	6.37
	373	0.00016	0.00044	9.01
	393	0.00009	0.00028	6.11

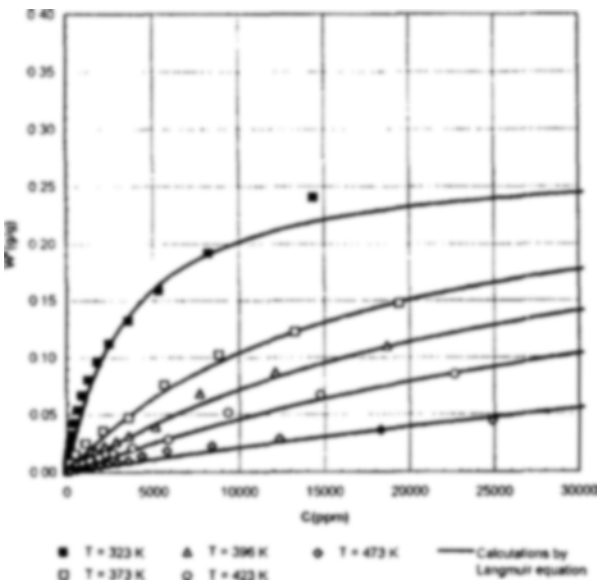

Fig. 1. The comparable plot of calculated values by Langmuir correlation with experimental data for the adsorption of dichloromethane.

The values of A and B decrease with increasing temperatures for both adsorbates. It means that the adsorbent has higher maximum loading and adsorption affinity at lower temperatures.

Fig. 1 shows the Langmuir isotherm fits of dichloromethane to the experimental data for this activated carbon pellet. The Langmuir isotherm appears to fit the data reasonably well. Furthermore, the maximum capacities of this carbon pellet is seen to be higher than that of two different kinds of com-

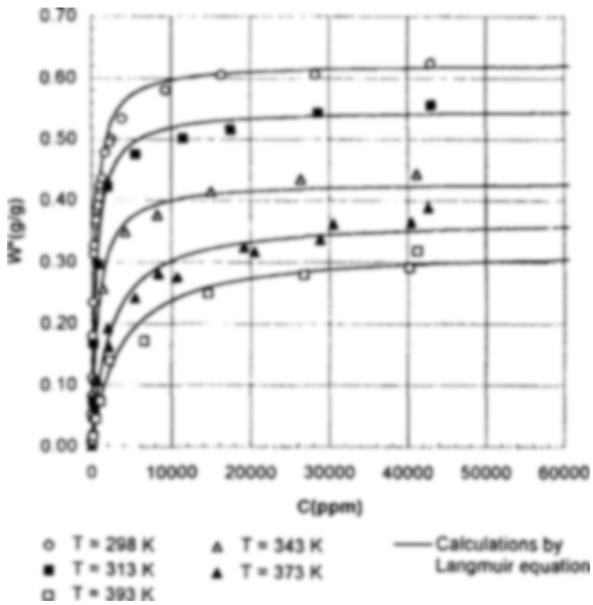

Fig. 2. The comparable plot of calculated values by Langmuir correlation with experimental data for the adsorption of 1,1,2-trichloro-2,2,1-trifluoroethane.

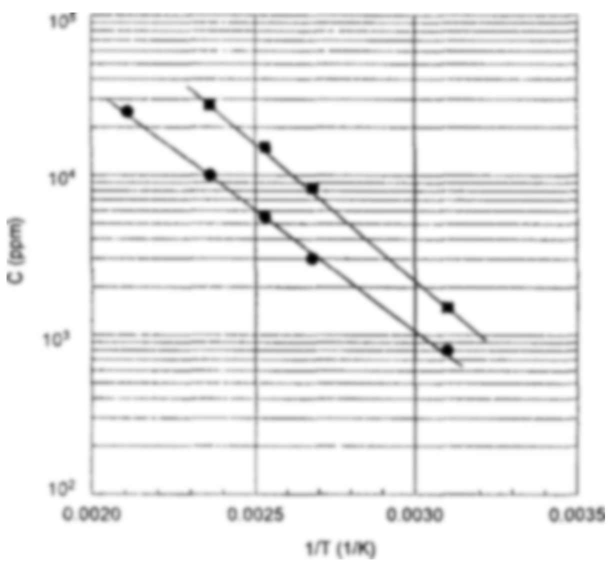

Fig. 3. Isosteric heats of adsorption of dichloromethane on the activated carbon pellet (●: q=7.04 kcal/mol at W=0.05 g/g, ■: q=7.75 kcal/mol at W=0.1 g/g).

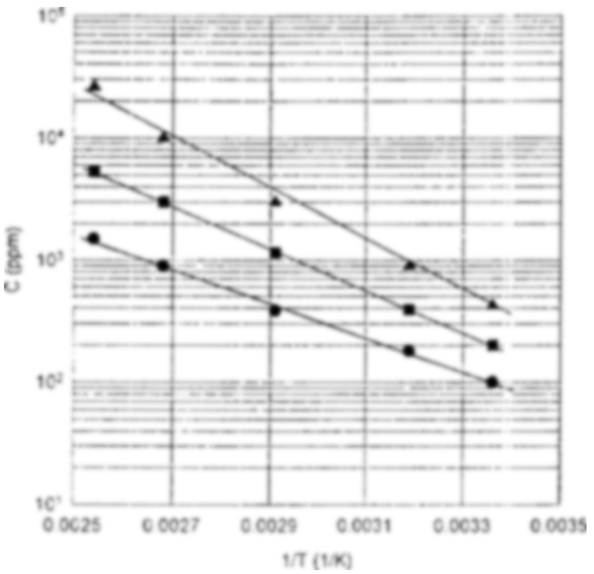

Fig. 4. Isosteric heats of adsorption of 1,1,2-trichloro-2,2,1-trifluoroethane on the activated carbon pellet (●: q=6.96 kcal/mol at W=0.1 g/g, ■: q=7.94 kcal/mol at W=0.2 g/g, ▲: q=9.68 kcal/mol at W=0.3 g/g).

mercial granular activated carbons (GACs) for dichloromethane adsorption reported in Chang' study [Tsai and Chang. 1994].

Fig. 2 illustrates the comparison of calculated values by Langmuir correlation with experimental data of 1,1,2-trichloro-2,2,1-trifluoroethane. Experimental data agree with the calculated values within 9% error.

The isosteric heats of adsorption were calculated at constant adsorption loading from the following relationship:

$$q=-R\cdot\left[\frac{\partial(\ln C)}{\partial(1/T)}\right]_W \tag{2}$$

Fig. 3 and Fig. 4 illustrate the isosteric heats of adsorption for two halogenated chemicals at constant loading with the variations of coverage. This figures show that the isosteric heats of adsorption for the two chemicals on the activated carbon pellet are slightly increasing with the amount of two adsorbates adsorbed per unit mass of the activated carbon pellet.

The isosteric heats of adsorption for two adsorbates on the activated carbon pellet are of the same order of magnitude as the heats of condensation [Benning and McHarness, 1934]. It may be considered that the adsorption of two chemicals on this activated carbon pellet is due primarily to physical forces.

CONCLUSION

It is suggested that this activated carbon pellet is very useful for adsorption of dichloromethane and 1,1,2-trichloro-2,2,1-trifluoroethane. Particularly, this pellet-type carbon merit the commercial attention, because of its regular size and hardness.

It was found that the experimental data of two halogenated carbons are well expressed by Langmuir correlation.

The isosteric heats of adsorption for two adsorbates on the activated carbon pellet were evaluated. Therefore, It may be considered that the adsorption of two chemicals on this activated carbon pellet is due primarily to physical forces.

NOMENCLATURE

A : Langmuir parameter in Eq. (1) [ppm^{-1}]
B : Langmuir parameter in Eq. (1) [ppm^{-1}]
C : concentration of adsorbate vapors [ppm]
q : isosteric heats of adsorption [kJ/mol]
R : gas constant [kJ/(mol·K)]
T : temperature [K]
W^* : mass of adsorbed material in equilibrium [g/g]

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