Study on adsorption properties of non-polar gases on porous materials in electric field

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Abstracts

Porous materials have high application values in practices like adsorbing harmful gases. However, the adsorption capacity on a certain kind of porous material is subject to its porous structure and the adsorption efficiency will decrease when the adsorption reaches its limit. The conjecture is that an external electric field can polarize non-polar gas molecules and van der Waals forces change, which results in the increase of the adsorption capacity on a certain kind of porous material per unit mass.

Proceeding from the BET theory in physical chemistry and the theory of intermolecular potential energy in structural chemistry, the thesis discusses how the external electric field polarizes non-polar molecules and affects intermolecular potential energy. A mathematical model is built on these relations and the BET theory.

Through a series of adsorption experiments at different electric field intensities, the mathematical model is initially validated and adjusted and the parameters are calculated. Due to the limited experimental conditions, the thesis only discusses the physical adsorption of non-polar gas molecules like CO_2 on silica aerogel. The experiment result turns out that effected by the external electric field, the adsorption capacity of CO_2 on silica aerogel per unit mass increases significantly, and the specific relation between adsorption capacity and electric field intensity accords with the model.

A further conjecture is raised to explore the selective adsorption of different gases. An interval in which the adsorption capacity changes significantly with electric field intensity is calculated. As electric field has different effect on the intermolecular potential energy of different gases molecules, the interval is supposed to vary with different types of gases, which shows the possibility to make selective adsorption of mixed gases by changing electric field intensity. As a practical idea to improve adsorption capacity and selective adsorption ability, the outcome of the thesis will be of value in aspects like environmental protection and chemical production.

Key words: porous materials, adsorption, electric field, adsorption capacity, selectivity.

Statement of Originality

The research process and result of this team are conducted and derived under the guidance of the instructor. Other than the referenced content and the acknowledged sources, this paper does not include any published findings by this group or any other researchers. If there is any inaccuracy, this team is accountable for all liabilities.

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Contents

1. Introduction

1.1 Backgrounds

Nowadays, harmful gases have caused serious damage to the environment. Porous materials such as activated carbon and aerogel, which are excellent gas adsorbents, can be used to adsorb harmful gases and particles for centralized treatments [1, 2]. Activated carbon has been widely used in adsorption of harmful gases in household needs. If adsorption capacities and efficiencies of activated carbon and aerogel can be increased substantially, it will show great significance of environmental protection in fields like controlling industrial waste gases and car exhausts. As porous materials can adsorb different components of mixed gases, if the absorbed harmful gases, like SO_2 and NO_2, can be separated and recycled, it can create remarkable economic benefits. From these perspectives, the thesis mainly discusses problems of two stages. The first one is how to improve the adsorption capacity of porous materials by adding external factors. The second one is to explore whether the external factor can make the adsorption into a selective process.

Considering how to improve adsorption capacity, the first thought is to find some kind of material with better adsorption ability. Aerogel has extremely low density and high adsorption property, which proves itself an ideal adsorption material [3]. Nowadays, the synthesis of aerogel is developing constantly and the production cost is reducing. This new material begins to show its advantage of application values [4, 5, 6, 7]. However, the adsorption capacity of a certain kind of porous material is subject to its porous structure and the efficiency decreases when the adsorption reaches its limit. Besides using better porous materials, to promote adsorption and inhibit desorption by adding external factors is another method. Common ways to improve adsorption include reducing temperature, increasing pressure, etc. However, considering that it requires strict conditions and costs a lot to do these, it cannot make a positive impact on the economic benefits to have massive introduction of these ways. After a series of experiments, the result shows that the external electric field can be used to polarize non-polar gas molecules, which changes intermolecular forces and then improve the adsorption capacity and efficiency. Because the external electric field only applies work to molecules in the adsorption process and does not need strict conditions like low temperature or high pressure, compared with the existing ways, the method to add an external electric field can make adsorption more efficient with lower costs while it benefits both in economically and environmentally.

As for selective adsorption, by studying the effect of electric field intensity on adsorption, the goal is to find an interval of electric field intensity in which the adsorption capacity changes significantly with the changing of electric field intensity. Because intermolecular forces are different between different kinds of gas molecules, and different gases are affected differently by the external electric field, the adsorptions of different gases on a certain kind of porous material change significantly in different intervals. In practice, mixed harmful gases can be adsorbed systematically and separated preliminarily by controlling electric field intensity.

Adsorption and intermolecular potential energy are important contents in physical chemistry of surfaces and structural chemistry. Proceeding from the existing BET theory and the theory of intermolecular potential energy [8, 9, 10, 11], the thesis explores how the deviation between the center of the positive and negative charge in a non-polar molecule, like a CO_2, SO_2 or NO_2 molecule, will be affected by the external electric field. Then the conjecture is proved by the relation between intermolecular potential energy and electric field intensity, which is deduced based on the theory of intermolecular potential energy. After that, a basic mathematical model to describe the relation is built based on the BET theory. Afterwards, the experimental results draw the adsorption isotherms of CO_2 on silica aerogel in no external electric field and in different electric field intensities. The isotherms can be fit with the mathematical model well. Also, the interval of electric field intensity in which the adsorption capacity changes significantly can be calculated, which gives a further improvement to the conjecture about selective adsorption. Due to the limitation of experimental conditions, the thesis can only discuss the physical adsorption of non-polar gas molecules CO_2 on silica aerogel and activated carbon, so as to provide a general idea and method to study the adsorption on other porous materials of other non-polar gases, such as NO_2 or SO_2.

1.2 Activated carbon and aerogel

Activated carbon has been commonly used as porous solid adsorbent in many fields like petrochemical production, power industry, chemical production and food industry, because of its large specific surface area and strong ability to adsorb ions in solutions and gas molecules. Activated carbon is also widely used for the purification of air or water in home lives [1, 2].

Aerogel is a kind of solid porous material which has extremely low solid density [3, 4]. Aerogel can be synthesized by many kinds of raw materials, such as silicone, carbon, sulfur, metal oxide, metal, etc. Aerogel can also be used as heat insulating material, acoustic delay material, and a new kind of gas filter material, etc. [4].

Fig.1.2-1 Activated carbon

Fig.1.2-2 Silica aerogel

As it is not safe to apply the parallel plate capacitor to any stricter conditions in the series of experiments, the pre-experiment and the experiments later on is all carried out at the temperature of ice water mixture. The pre-experiment aims to compare the adsorption abilities of activated carbon and silica aerogel, and the latter has a better performance. The later experiments will mainly focus on the adsorption on silica aerogel, so as to study the adsorption properties of porous materials [5, 6, 7].

1.3 The introductions of physical adsorption, the BET theory and the Freundlich isotherm equation

The forces applied to the atoms on the surface of solid adsorbent by the atoms surrounding, are asymmetric, that is, the forces exerted by the atoms on the surface are unsaturated. There is residual force field, which make the adsorbent can adsorb gas or liquid atoms. As the reactions between adsorbate molecules and adsorbent surface are of different kinds, the adsorption process can be classified as physical adsorption (physisorption) without selectivity or chemical adsorption (chemisorption) with selectivity. Physical adsorption can exist between any gas and solid, and can be a monolayer or multilayer process. There is no electron transfer, no formation and destruction of chemical bonds, and no rearrangement of atoms in the process of physical adsorption. Physical adsorption is caused only by van der Waals forces. The adsorption process on silica aerogel is mainly physical adsorption.

The adsorption isotherms worked out in previous experiments have showed that most of the adsorption processes of gases, especially physical adsorption, are multilayer adsorption rather than monolayer adsorption. So that means after one layer of molecules are adsorbed on the surface of the adsorbent, due to the van der Waals forces of the adsorbed gas molecules themselves, there will be multilayer adsorption. When the adsorption process reaches the equilibrium, the total adsorption capacity is the sum of the adsorption capacities of all layers. It can be testified by the experimental results in the following parts, that the equation of the BET theory with two constants V_m and C:

$$\frac{V}{V_m} = \frac{C_p}{(p_0 - p)(1 - \frac{p}{p_0} + C\frac{p}{p_0})} \qquad (1.3\text{-}1)$$

and the equation with three constants can be used in the physical adsorption of non-polar gases on aerogel. In the equation, V represents the adsorbed gas capacity at the equilibrium pressure p, V_m stands for monolayer adsorption capacity, p_0 stands for the saturated vapor pressure at certain temperature, and C is a constant related to adsorption heat. Considering the type of adsorption on mesopore materials and the required ratio $\frac{p}{p_0}$from0.05to0.35, the equation of the BET theory with two constants is adopted in the theoretical deduction and the analysis of experiment data [8,9, 10].

As it needs no consideration about saturated adsorption to use the Freundlich isotherm equation, and the equation can be applied to a wide range of systems, it is widely used in physical adsorption, chemical adsorption and solution adsorption. The empirical formula is

$$q = kp^{\frac{1}{n}} \tag{1.3-2}$$

in which q represents the capacity of the gas adsorbed by unit mass of solid, p is the equilibrium pressure of gas, while $k$and $n$are constants numbers at certain temperature in a certain system. Because of the limited experimental conditions, it is unavailable to meet the required ratio $\frac{p}{p_0}$ of the BET theory. After a pre-experiment at low temperature, it is concluded that the adsorption of CO_2 on silica aerogel can be fitted by the Freundlich isotherm equation when $\frac{p}{p_0}$ is in the range from 0.01 to 0.203. Therefore, the Freundlich isotherm equation is used to fit the data of the series of experiments at 0℃, so as to predict the adsorption capacity of CO_2 on silica aerogel at the pressure of 1350-1950 mmHg (when $\frac{p}{p_0}$ is in the range from0.051 to 0.075 and in the required range of the BET formula).

1.4 van der Waals force and intermolecular potential energy

In physical adsorption, the adsorption process is caused by van der Waals forces, which are weaker than covalent bonds and can change in a wide range. The Lennard – Jones potential model approximately demonstrates that the intermolecular force will be attractive when the distance between two molecules is long, and that the intermolecular force will be repulsive when the distant is short. In the early 20th century, Keesom, Debye and London put forward theories that van der Waals force includes electrostatic interaction, induction interaction, dispersion interaction.

Electrostatic interaction, which is also referred to as Keesom interaction, exists only among molecules which possess permanent dipole moments. The Electrostatic interaction depends on the size of the molecules, the intermolecular distance, and temperature. To set aside the orientations of molecules, the average energy of the electrostatic interaction between two molecules which have respective dipole moments of μ_A and μ_B at a distance of r can be represented as:

$$E_{\mu_A\mu_B} = \frac{-2{\mu_A}^2{\mu_B}^2}{3r^6kT(4\pi\varepsilon_0)^2} \tag{1.4-1}$$

Induction interaction exists between a molecule with permanent dipole moment and other molecules. There is non-zero electric field around a polar molecule, which can change the distribution of charges and induce dipole moments in neighboring polar or non-polar molecules. The induced dipole moments align with the electric field, that is, the dipole moment of the polar molecule, which causes induction interaction between two molecules. The average energy of the induction interaction between a molecule with the dipole moment ofμ_A and another molecule with the polarizability ofα_B can be represented as:

$$\mathrm{E}_{\mu_A\alpha_B} = \frac{-{\mu_A}^2\alpha_B}{r^6(4\pi\varepsilon_0)^2} \tag{1.4-2}$$

Dispersion interaction exists among all molecules. Although a non-polar molecule does not have permanent dipole moment, the movement of the electrons in the molecule makes the distribution of charges change constantly, which results in an instantaneous dipole moment. The instantaneous dipole moment contributes to an electric field, and can induce dipole moments in neighboring molecules. The induced dipole moments react against the original molecule, and result in a further dipole moment in it. Like this, the interaction among induced dipole moments result in further dipole moments, and they are ordered in the same direction. The attraction among them contribute to dispersion interaction. The average energy of the dispersion interaction between two molecules which have respective ionization energy of $I_1$and I_2 and polarizability of$\alpha_A$and α_B at a distance of r can be represented as:

$$E_{\alpha_A\alpha_B} = -\frac{3}{2}\left(\frac{I_1I_2}{I_1+I_2}\right)\frac{\alpha_A\alpha_B}{r^6(4\pi\varepsilon_0)^2} \tag{1.4-3}$$

These three interactions constitute to the van der Waals attraction. In the adsorption process, the attraction will be dominant. [11]

2. Theoretical deduction

2.1 Molecular polarization in electric field

The CO_2 molecule is taken as an example. According to the VSEPR theory, without external electric field, theCO_2molecule is a non-polar molecule with linear structure (Fig.2.1-1) and it is a non-polar molecule. There is no lone electron pair in the central carbon atom.

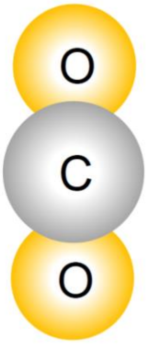


Fig.2.1-1 Schematic sketch of CO_2 molecule

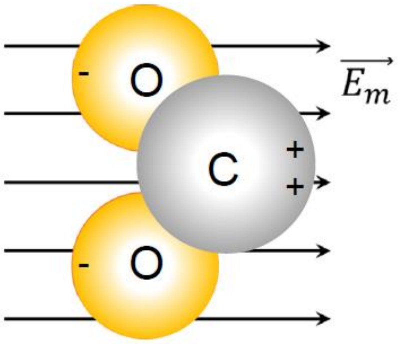


Fig.2.1-2 Schematic sketch of CO_2 molecule in electric field

The molecule is polarized in the electric field $\overrightarrow{E_m}$(Fig.2.1-2).As oxygen has stronger atomic electronegativity than carbon, positive charge is distributed in the central carbon atom and negative charge is distributed in the oxygen atoms.

The molecule is abstracted as a sphere with the radius of R(Fig.2.1-3). Positive charge of q_1 is at the centre of the sphere and negative charge of q_2 are well distributed over the whole sphere.

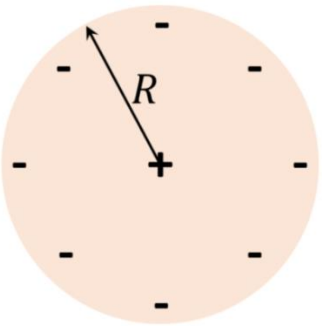


Fig.2.1-3 Charge distribution in the abstracted molecule

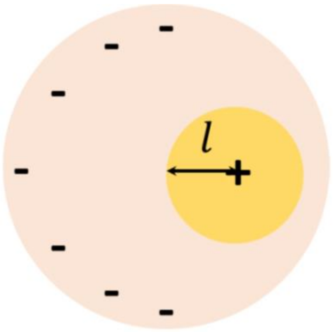


Fig.2.1-4 Charge distribution in the abstracted polarized molecule

In electric field, the positive charge centre deviates (Fig.2.1-4). If the distribution of negative charge is seen as a uniformly charged sphere with the radius of R, and the positive charge is seen as a point charge, the deviation between the positive point charge and the sphere centre is l. From the equilibrium of electrostatic forces, the following equation can be derived:

$$q_1 E_m = \frac{q_1 q_2 l}{4\pi\varepsilon_0 R^3} \tag{2.1-1}$$

where q_1 , q_2 are absolute values. Hence $q_1 = q_2$, and

Then

$$l = \frac{4\pi\varepsilon_0 E_m R^3}{q_1} \tag{2.1-2}$$

The dipole moment $\vec{\mu}$ of the polarized $\mathrm{CO_2}$ molecule is

$$\vec{\mu} = q_1 \vec{l} = 4\pi\varepsilon_0 R^3 \overrightarrow{E_m} = \alpha \overrightarrow{E_m} \tag{2.1-3}$$

where $\alpha$is the polarizability of the $\mathrm{CO_2}$molecule.[12]

$$\alpha = 4\pi\varepsilon_0 R^3 \tag{2.1-4}$$

As for an $\mathrm{O_2}$ molecule, a similar model can be adopted to describe the deviation between the positive charge centre and the negative centre.(Fig.2.1-5),

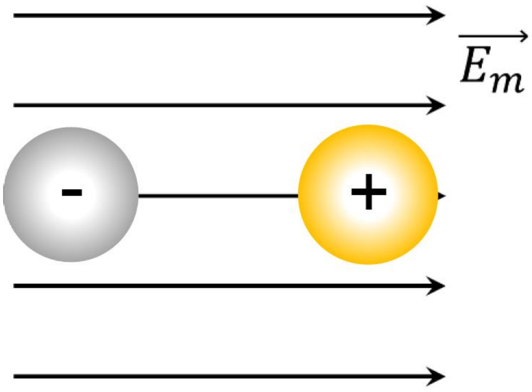


Fig.2.1-5 Charge distribution in the polarized $\mathrm{O_2}$ molecule

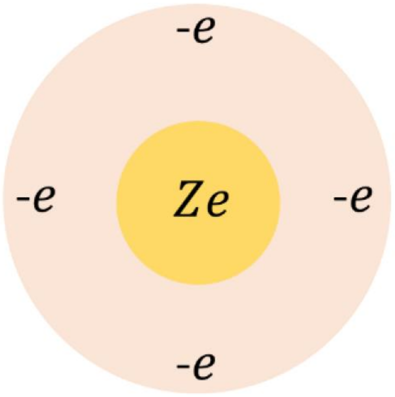


Fig.2.1-6 Charge distribution in an atom

As for a single atom, we consider the nuclear as the positive charge center and the electron cloud as the negative charge, in which we neglected the shape of the electron cloud (Fig.2.1-6).Then we draw the same conclusions.

2.2 The change of intermolecular potential energy in electric field

The adsorption of CO_2 on silica aerogel is physical adsorption, which is relevant to intermolecular interactions, mainly the van der Waals forces. We study the effect of the polarization on the intermolecular potential energy.

Van der Waals forces consist of orientation interaction (Keesom force), induction interaction (Debye force) and dispersion interaction (London force). As CO_2 molecules are polarized in electric field, all three interactions contribute to the change of intermolecular potential energy.

(1)Orientation interaction

The force originates from the attraction between permanent dipoles (dipolar molecules) and is temperature dependent. The averaged potential energy of orientation interaction is given by the following equation*(1.4-1)*:

$$E_{\mu_A \mu_B} = \frac{-2\mu_A^2 \mu_B^2}{3r^6 kT(4\pi\varepsilon_0)^2}$$

where μ_A and μ_B are the respective dipole moments of molecule A and B, T is thermodynamic temperature, r is the distance between two molecules and k is Boltzmann constant. According to the previous deduction, it can be derived that*(2.1-3)* [13]

$$\vec{\mu} = \alpha \overrightarrow{E_m}$$

in which *(2.1-4)*

$$\alpha = 4\pi\varepsilon_0 R^3$$

Thus

$$E_{Keesom} = \frac{-32(\pi\varepsilon_0 R_1^3 R_2^3)^2}{3kr^6} \cdot \frac{E_m^4}{T} \propto E_m^4 \qquad (2.2\text{-}1)$$

in which it is known that the potential energy of Orientation interaction is proportional to E_m^4.

(2)Induction interaction

Induction interaction arises from interactions between rotating permanent dipoles and from the polarizability of atoms and molecules (induced dipoles).A molecule with permanent dipole can induce a dipole in a similar neighboring molecule and cause mutual attraction.

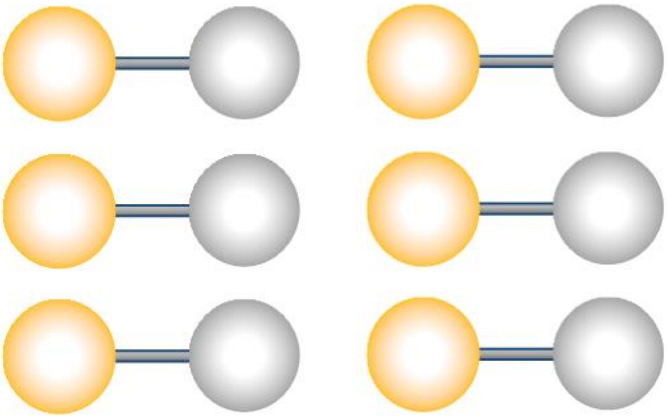


Fig.2.2-1 Charge distribution of abstracted polarized molecules (orange spheres represent positive charge centres, grey spheres represent negative charge centres)

The averaged potential interaction is given by the following equation*(1.4-2)*.

$$E_{\mu_A \alpha_B} = \frac{-\mu_A^2 \alpha_B}{r^6 (4\pi\varepsilon_0)^2}$$

from which, the following equation can be derived:

$$E_{Debye} = \frac{-\alpha_A^2 \alpha_B}{r^6 (4\pi\varepsilon_0)^2} \cdot E_m^2 \propto E_m^2 \qquad (2.2\text{-}2)$$

Thus the potential energy of Induction interaction is proportional to E_m^2.

(3)Dispersion interaction

Dispersion interaction arises due to the non-zero instantaneous dipole moments of all atoms and molecules. Such polarization can be induced either by a polar molecule or by the repulsion of negatively charged electron clouds in non-polar molecules.

The averaged potential energy of dispersion interaction is given by the following equation*(1.4-3)*.

$$E_{\alpha_A \alpha_B} = -\frac{3}{2} \cdot \left(\frac{I_1 I_2}{I_1+I_2}\right) \cdot \frac{\alpha_A \alpha_B}{r^6 (4\pi\varepsilon_0)^2}$$

where $I_1$and $I_2$are the ionization potentials of molecule A and B.

Again, we have

$$E_{London} = -\frac{3}{2} \cdot \left(\frac{I_1 I_2}{I_1+I_2}\right) \cdot \frac{R_1^3 R_2^3}{r^6} \qquad (2.2\text{-}3)$$

Therefore, the potential energy of Dispersion interaction is irrelevant to the electric field E_m.

Above all, when the external electric field intensity E_m increases, the intermolecular potential energy increases.

2.3The change of adsorption capacity in electric field

At certain temperature, intermolecular potential energy can be described as:

$$E = E_{Keesom} + E_{Debye} + E_{London} = AE_m^4 + BE_m^2 + C_0 \qquad (2.3\text{-}1)$$

Where$A$,$B$and$C_0$are constants relevant to the molecule itself.

When electric field is not applied, only dispersion interaction exists between two non-polar molecules. From *(2.2-8)*, dispersion interaction is irrelevant to the external electric field. Thus, the intermolecular potential energy $E_0$is given by:

$$E_0 = E_{London} = C_0 \qquad (2.3\text{-}2)$$

Known from isochoric thermal effect, with no expansion work, the change of adsorption heat equals to the change of the thermodynamic energy, that is, the change of the intermolecular potential energy.[14][15]

Hence

$$\Delta E_{adsorption} = E - E_0 = AE_m^4 + BE_m^2 \qquad (2.3\text{-}3)$$

As the adsorption on silica aerogel is physical adsorption, we apply the equation of the BET theory with two constants to build our model, which is

$$\frac{V}{V_m} = \frac{Cx}{(1-x)(1-x+Cx)} \qquad (2.3\text{-}4)$$

where $V$is the volume of the adsorbed gas, $V_m$is the monolayer adsorbed gas quantity, and x and C are given by:

$$x = \frac{p}{p_0} \tag{2.3-5}$$

$$C = \frac{a_1 b_n}{a_n b_1} e^{\frac{E-E_L}{RT}} = D e^{\frac{E-E_L}{RT}} \tag{2.3-6}$$

where p is the equilibrium pressure and p_0 is the saturated pressure of adsorbate at certain temperature, a_1 and b_1 are constants corresponding to monolayer adsorption. a_n and b_n are constants corresponding to the n layer adsorption, which varies with electric field intensity, E corresponds to adsorption heat and E_L is liquefaction heat.

With electric field , the adsorption heat changes into $(E + \Delta E_{adsorption})$, so the constant C changes into C_1, that is:

$$C_1 = D_1 e^{\frac{E+\Delta E_{adsorption}-E_L}{RT}} \tag{2.3-7}$$

Hence

$$\frac{C_1}{C} = \frac{D_1}{D} e^{\frac{\Delta E_{adsorption}}{RT}} = \frac{a_n b'{}_n}{a'{}_n b_n} e^{\frac{AE_m^4+BE_m^2}{RT}} = e^{xE_m^4+yE_m^2} \cdot e^{\alpha' E_m^4+\beta' E_m^2} = e^{\alpha E_m^4+\beta E_m^2} \tag{2.3-8}$$

The adsorption equation is

$$\frac{V_1}{V_m} = \frac{C_1 x}{(1-x)(1-x+C_1 x)} \tag{2.3-9}$$

where V_1 is the new adsorption capacity in electric field.

By $\frac{(2.3-4)}{(2.3-9)}$, it can be derivated that

$$\frac{V}{V_1} = \frac{C(1-x)+CC_1 x}{C_1(1-x)+CC_1 x} \tag{2.3-10}$$

Substitute *(2.3-8)* to *(2.3-10)*, the equation goes:

$$\frac{V}{V_1} = \frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x} \tag{2.3-11}$$

The graph of the equation is drawn by mathematical software (Fig 2.3).

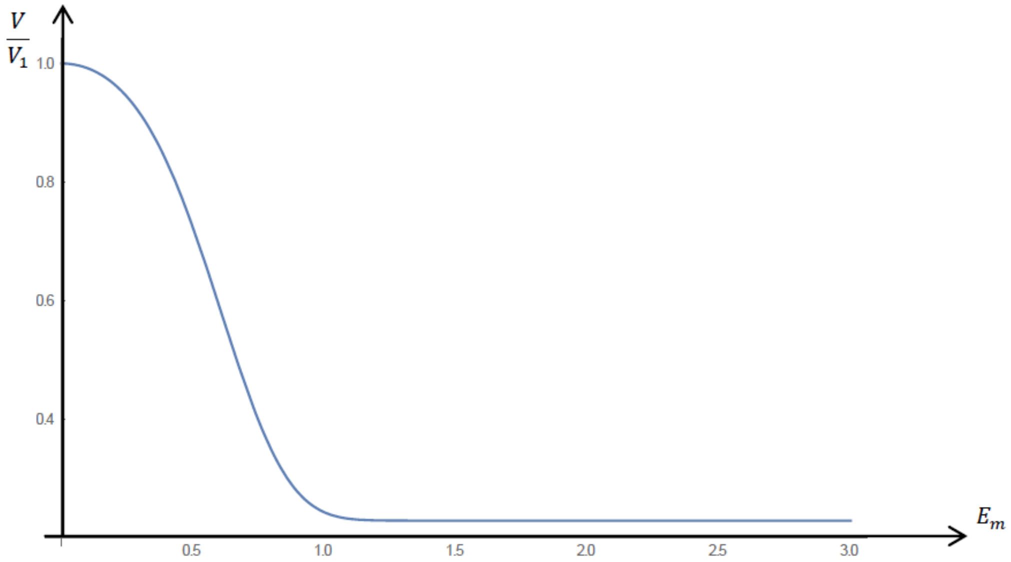


Fig.2.3 Relation between $\frac{V}{V_1}$ and electric field intensity

The graph shows that at certain pressure and temperature, as the electric field intensity increases, $\frac{V}{V_1}$decreases, which suggests that the saturation adsorption capacity increases with electric field intensity.

2.4The relation between adsorption capacity and pressure in electric field

From *(2.3-11)*, we have

$$\frac{V}{V_1} = \frac{(1-x) + Ce^{\alpha E_m^4 + \beta E_m^2}x}{e^{\alpha E_m^4 + \beta E_m^2}(1-x) + Ce^{\alpha E_m^4 + \beta E_m^2}x}$$

At certain temperature and electric field intensity, the graph can be drawn to describe how $\frac{V}{V_1}$ changes (Fig 2.4-1):

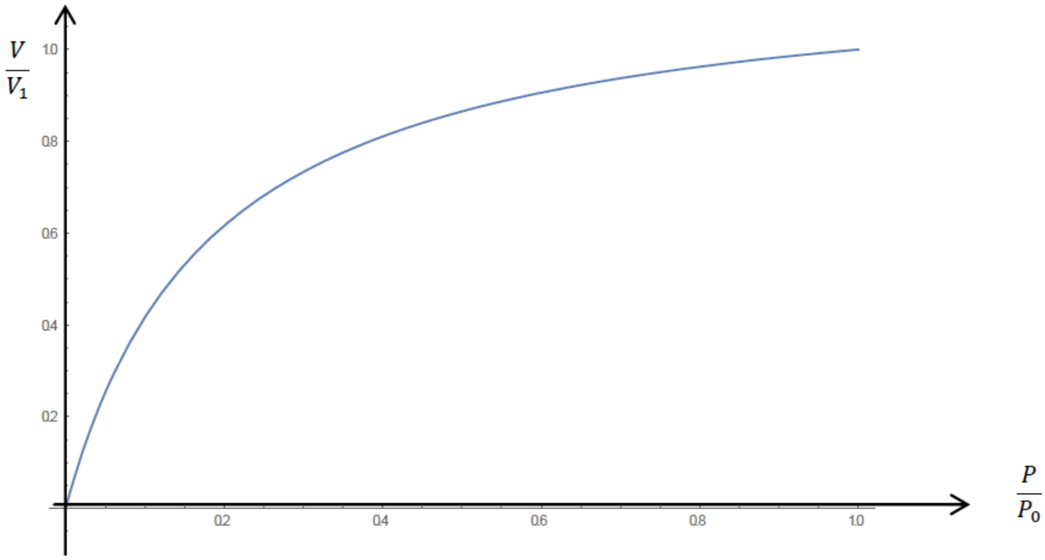


Fig.2.4-1 The relation between ratio of adsorption capacity and pressure

As $\frac{p}{p_0}$, $\frac{V}{V_1}$ increases, the effect of the electric field weakens.

As for the adsorption of one kind of gases at certain temperature, Fig 2.4-2 can show the comprehensive effect of the electric field intensity and the pressure.

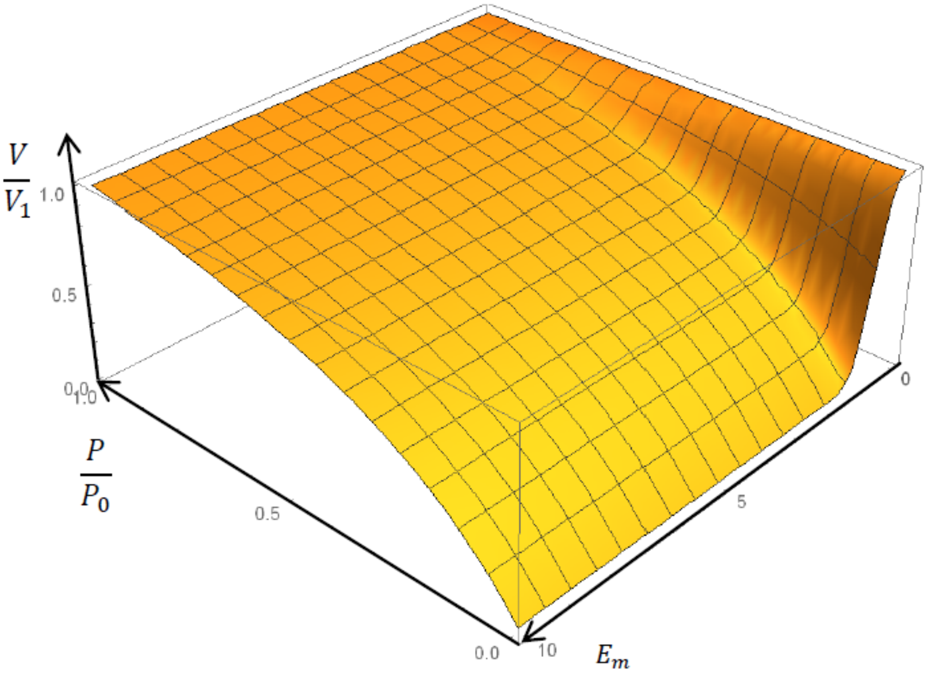


Fig.2.4-2 The comprehensive effect of electric field intensity and pressure

2.5The relation between adsorption capacity and temperature in electric field

From *(2.3-8)* $\frac{AE_m^4+BE_m^2}{RT}=\alpha E_m^4+\beta E_m^2$, the following equation can be derivated:

$$\alpha E_m^4+\beta E_m^2=\frac{A_1E_m^4+B_1E_m^2}{T} \qquad (2.5\text{-}1)$$

Substitute *(2.5-1)* to the equation *(2.3-11)*$\frac{V}{V_1}=\frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$, and the equation goes

$$\frac{V}{V_1}=\frac{(1-x)+Ce^{(A_1E_m^4+B_1E_m^2)/T}x}{e^{(A_1E_m^4+B_1E_m^2)/T}(1-x)+Ce^{(A_1E_m^4+B_1E_m^2)/T}x} \qquad (2.5\text{-}2)$$

At certain pressure and electric field intensity, the graph can be drawn to describe how $\frac{V}{V_1}$ changes(Fig.2.5-1):

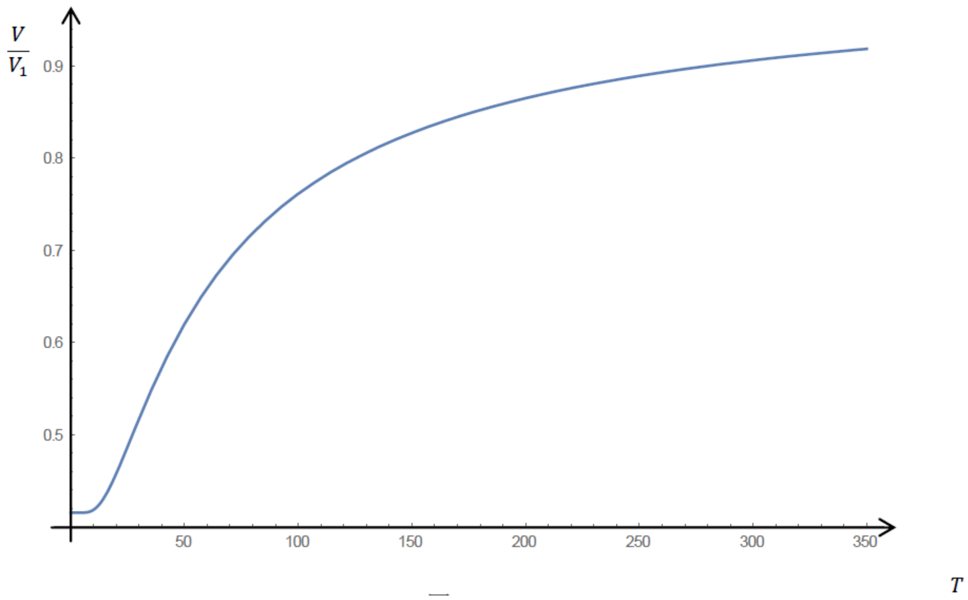


Fig.2.5-1 The relation between ratio of adsorption capacity and temperature

As the figure shows, when temperature rises, $\frac{V}{V_1}$ rises, which suggests that the effect of electric field weakens.

At certain $\frac{p}{p_0}$, the comprehensive effect of temperature and electric field intensity is showed in the graph.

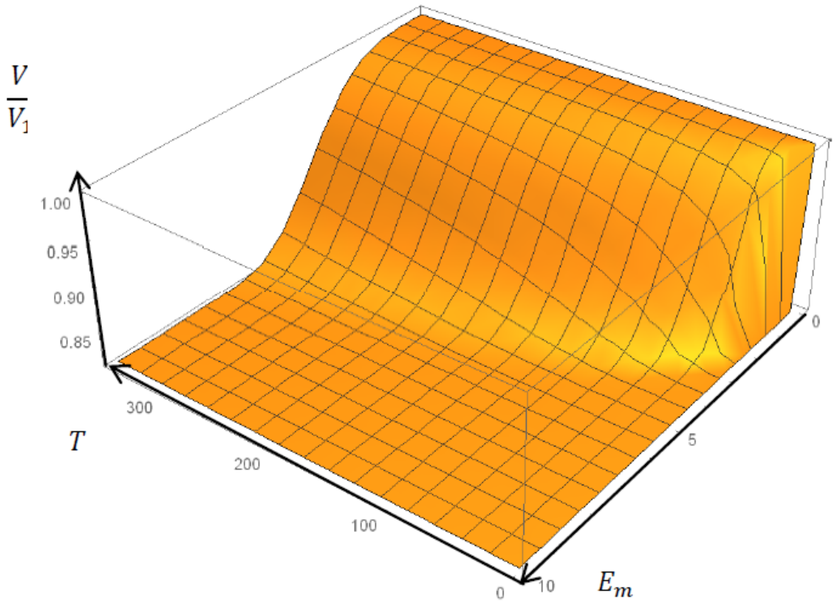


Fig.2.5-2 The comprehensive effect of electric field intensity and temperature

2.6The conjecture of selective adsorption

As the figure.2.3 shows, there is an interval of electric field intensity in which $\frac{V}{V_1}$ changes significantly. To study the interval, let

$$f(E_m)=\frac{V}{V_1}=\frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$$

The second derivative can describe the concavity and convexity of the function. The curve of $f''(E_m)$ is shown in figure.2.6-1.

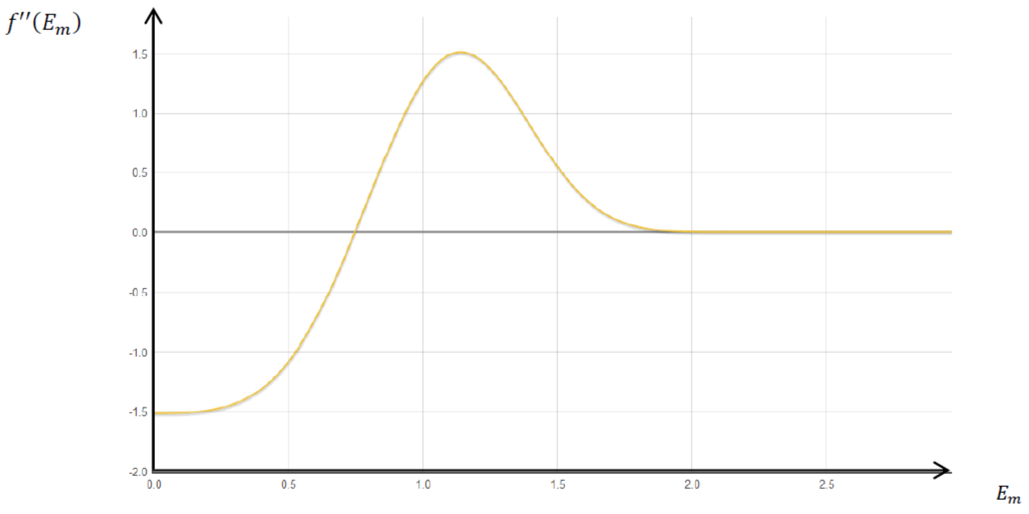


Fig.2.6-1 The figure of $f''(E_m)$

From figure.2.6.1, the two points of the interval are the two extreme value points of $f''(E_m)$ which can be figure out by solving $f'''(E_m)$.

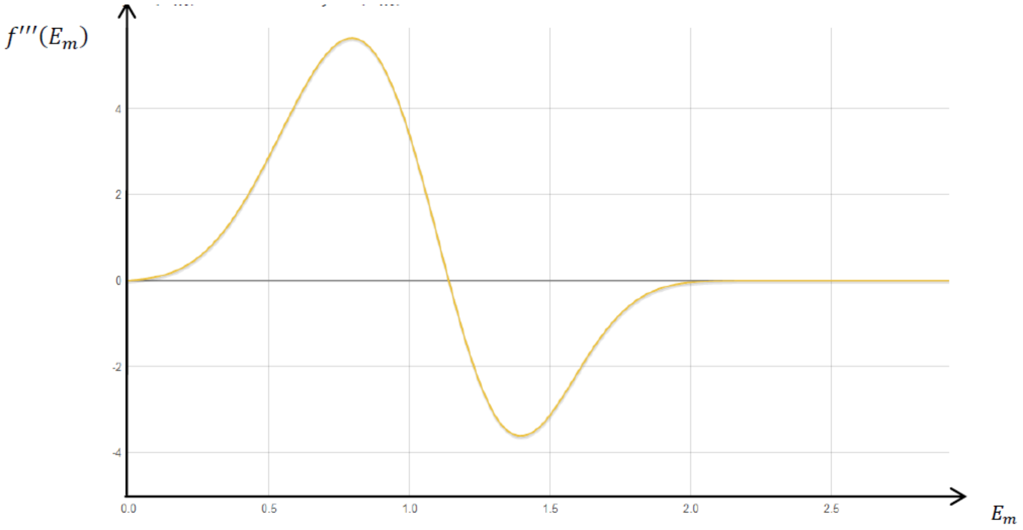


Fig.2.6-2 The figure of $f'''(E_m)$

Solve $f'''(E_m) = 0$, that is

$$\frac{\left(\left(\left(24a-12b^2\right)x+12b^2-24a\right)E+\left(\left(8b^3-96ab\right)x-8b^3+96ab\right)E^3+\left(\left(48ab^2-144a^2\right)x-48ab^2+144a^2\right)E^5+\left(96a^2bx-96a^2b\right)E^7+\left(64a^3x-64a^3\right)E^9\right)e^{-bE^2-aE^4}}{\left(c-1\right)x+1}=0$$

Figure out the two positive roots of the equation, E_{m1} and E_{m2}.The interval $[E_{m1}, E_{m2}]$ is the interval in which $\frac{V}{V_1}$ changes significantly.

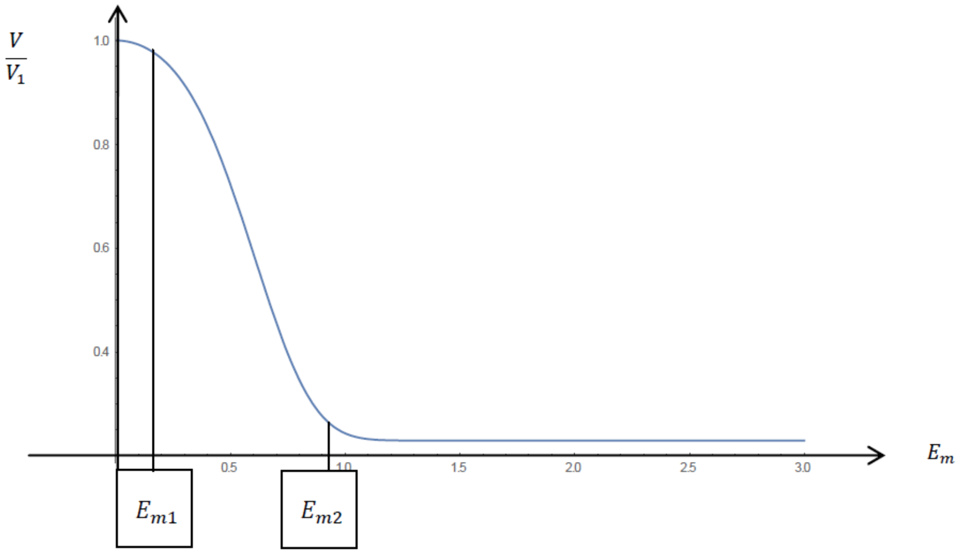


Fig.2.6-3 Electric field intensity interval[E_{m1},E_{m2}]

From the equation and the model, it is supposed that the interval is relevant to the type of the gas. With different intervals of different gases, the selective adsorption can be achieved by controlling electric field intensity. We can make the material adsorb one kind of gases more than the others by controlling the electric field intensity.

3. Experiments

3.1 Apparatus and preparation

Powdered silica aerogel(commercially available, degasification for 2 hours before experiment), parallel plate capacitor(plate spacing: 0.03 m), pure CO_2, insulated dewar, glass sample tube, student power supply(maximum voltage:15V), type ASAP2020 physical adsorption instrument(Micromeritics Company), circuit switch and wires.

Fig.3.1-1 Photo of experiment apparatus

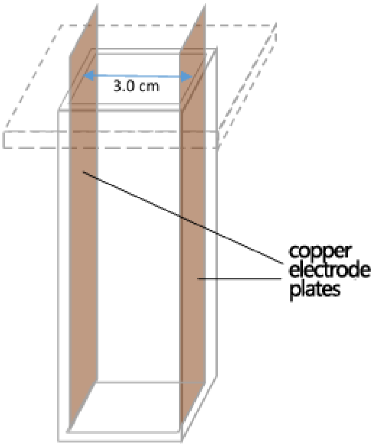


Fig.3.1-2 Parallel plate capacitor

3.2 Purpose and main procedures

Purpose: Through three series of adsorption experiment of CO_2 on silica aerogel in electric field (electric field intensity are 0 N/C, 333 N/C and 500 N/C), get the preliminary shape of adsorption isotherm and validate the equation which has been described above:

$$\frac{V}{V_1} = \frac{(1-x) + Ce^{\alpha E_m^4 + \beta E_m^2} x}{e^{\alpha E_m^4 + \beta E_m^2}(1-x) + Ce^{\alpha E_m^4 + \beta E_m^2} x}$$

Fit the curve and calculate the parameter α and β of the adsorption ofCO_2 on silica aerogel. Calculate the electric field intensity interval $[E_{m1}, E_{m2}]$ in which the adsorption capacity changes with electric field intensity significantly.

Main procedure: Degas the powdered silica aerogel sample in the sample tube for two hours before the experiment, seal it up and set aside. Prepare ice water mixture. Connect the circuit, examine for correctness and safety.

Insert the glass sample tube with degassed silica aerogel sample into the parallel plate capacitor. Put the device into the prepared ice water mixture. Turn off the circuit switch and begin the adsorption experiment of CO_2. The intake quantity of CO_2increases gradually, and the pressure in the sample tube increases gradually. Mark down the adsorption capacity of CO_2on silica aerogel at different pressures.

After the first set of experiment, degas the silica aerogel sample and repeat the first set of experiment. Average the data from the two processes.

Degas the aerogel sample again. Turn on the circuit switch and turn the voltage to about 15V, with corresponding field intensity of 500 N/C. Do the adsorption experiment of CO_2at this electric field intensity twice and average the data.

Similarly, turn the voltage to about 10V, with the corresponding electric field intensity of 333 N/C. Do the adsorption experiment of CO_2at this electric field intensity twice and average the data.

3.3 Data analysis

Set1. electric field intensity: 0N/C

Date:	7/26/2016	Analysis Adsorptive:	CO_2
Analysis Bath Temp.:	273.150 K	Thermal Correction:	Yes
Sample Mass:	0.1152 g	Equilibration Interval:	10 s
Cold Free Space:	29.0771 cm^3	Warm Free Space:	27.3372 cm^3
Low Pressure Dose:	None	Automatic Degas:	Yes

Isotherm Tabular Report

Absolute Pressure(mmHg)	Quantity Adsorbed (cm^3g STP)	Elapsed Time(h:min)
57.3135	0.4258	00:42
114.5944	0.7588	00:44
199.7228	1.1682	00:47
299.7799	1.5648	00:49
400.3297	1.9096	00:51
500.3494	2.2676	00:53
600.2151	2.6125	00:56
700.3969	2.8865	00:58
749.9164	3.1222	01:00

Known from 1.3, it is unavailable to meet the required ratio $\frac{p}{p_0}$ of the BET theory in our experiment. Therefore the Freundlich isotherm equation (1.3-2) is used to fit the data of the series of experiments at 0℃, so as to predict the adsorption of CO_2 on silica aerogel at the pressure of 1350.0000-1950.0000 mmHg (when $\frac{p}{p_0}$ is in the range from 0.051 to 0.075 and in the required range of the BET formula). The fitted data is shown in the following graph and tables.

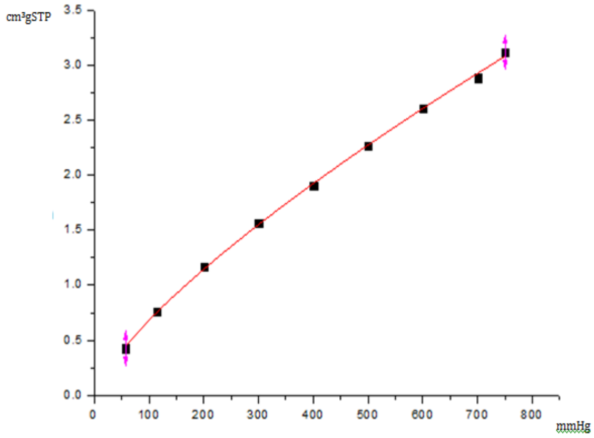


Fig.3.3-1 Original data and fitting result(0N/C)

$q = kp^{\frac{1}{n}}$		
	Value	Standard Error
k	0.02166	0.00145
n	1.33526	0.01923

Absolute Pressure(mmHg)	Quantity Adsorbed (cm^{3}g STP)	$\frac{p}{p_0}$
1350.0000	4.786534	0.051645
1450.0000	5.049673	0.055471
1550.0000	5.308291	0.059297
1650.0000	5.562749	0.063122
1750.0000	5.813363	0.066948
1850.0000	6.060404	0.070773
1950.0000	6.304113	0.074599

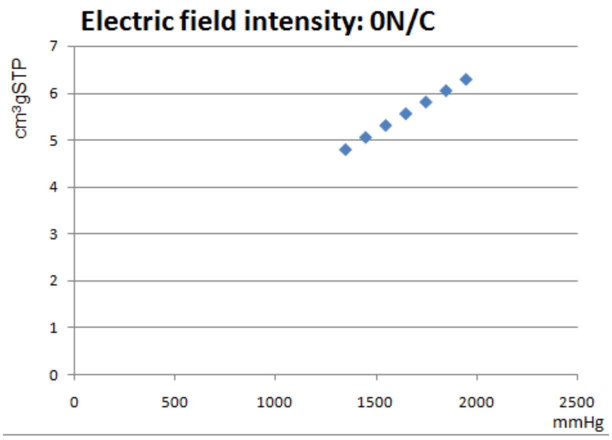


Fig.3.3-2 Calculated value of adsorption capacity(0N/C)

Set 2. electric field intensity: 500 N/C

Date: 7/27/2016

Analysis Adsorptive: CO_2

Analysis Bath Temp.: 273.150 K

Thermal Correction: Yes

Sample Mass: 0.1152 g

Equilibration Interval: 10 s

Cold Free Space: 29.0771 cm^3

Warm Free Space: 27.3372 cm^3

Low Pressure Dose: None

Automatic Degas: Yes

Isotherm Tabular Report

Absolute Pressure(mmHg)	Quantity Adsorbed (cm^3g STP)	Elapsed Time(h:min)
57.1610	0.6641	00:45
114.4192	1.0600	00:47
199.7953	1.5439	00:50
300.3064	2.0338	00:52
400.4131	2.4701	00:54
500.1577	2.8699	00:56
600.3221	3.2472	00:58
700.4536	3.6035	01:01
750.1388	3.7745	01:03

As set 1, the fitted data at the pressure of 1350.0000-1950.0000 mmHg (when $\frac{p}{p_0}$ is in the range from 0.051 to 0.075 and in the required range of the BET formula) is shown in the following graph and tables.

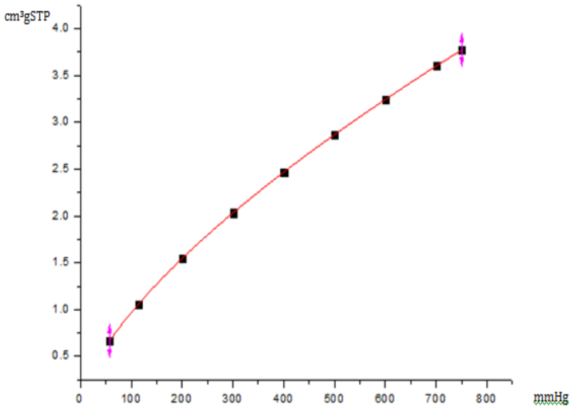


Fig.3.3-3 Original data and fitting result(500N/C)

$q = kp^{\frac{1}{n}}$		
	Value	Standard Error
k	0.04315	3.42901×10^{-5}
n	1.4806	2.81164×10^{-4}

Absolute Pressure(mmHg)	Quantity Adsorbed (cm^3g STP)	$\frac{p}{p_0}$	$\frac{V}{V_1}$
1350.0000	5.617678	0.051645	0.85204856
1450.0000	5.895502	0.055471	0.856529765
1550.0000	6.167173	0.059297	0.860733254
1650.0000	6.433210	0.063122	0.864692579
1750.0000	6.694064	0.066948	0.868435499
1850.0000	6.950122	0.070773	0.871985244
1950.0000	7.201725	0.074599	0.875361454

The data is fitted into the model $\frac{V}{V_1} = \frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$, where $x = \frac{p}{p_0}$. Let $y = \frac{V}{V_1}$ and $d = e^{\alpha E_m^4+\beta E_m^2}$ as the electric field intensity is a constant and get the fitting result which is shown in the following graphs and tables.

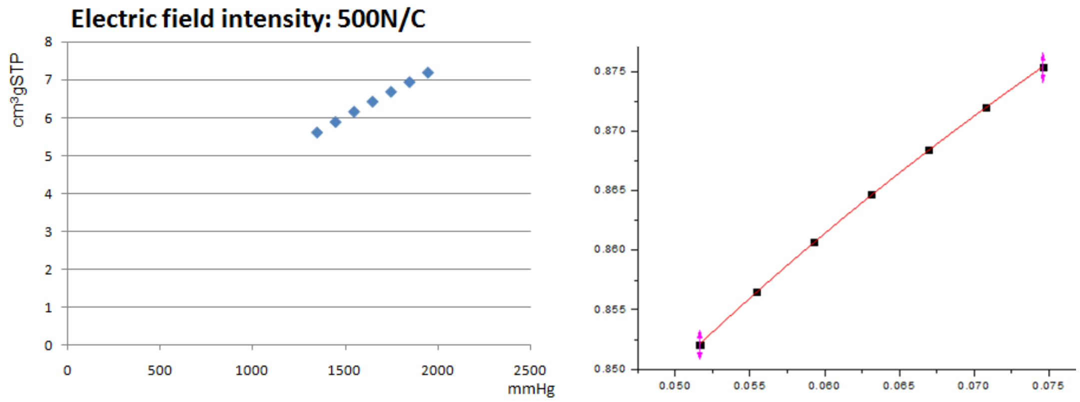


Fig.3.3-4 Calculated value of adsorption capacity(500N/C)

Fig.3.3-5 Fitting result of calculated value(500N/C)

$y=\frac{1-x+cdx}{d(1-x)+cdx}$		
	Value	Standard Error
C	11.71623	0.06364
D	1.31964	0.001

Set 3. electric field intensity: 333N/C

Date: 7/27/2016 Analysis Adsorptive: CO_2

Analysis Bath Temp.: 273.150 Thermal Correction: Yes

Sample Mass: 0.1152 g Equilibration Interval: 10 s

Cold Free Space: 29.0771 cm^3 Warm Free Space: 27.3372 cm^3

Low Pressure Dose: None Automatic Degas: Yes

Isotherm Tabular Report

Absolute Pressure(mmHg)	Quantity Adsorbed (cm^3g STP)	Elapsed Time(h:min)
56.97312	0.5067	00:46
114.3700	0.8501	00:48
199.6944	1.2894	00:50
299.6120	1.7448	00:52
400.2473	2.1660	00:55
500.3420	2.5583	00:57

600.2507	2.9297	00:59
700.4150	3.2874	01:01
750.0858	3.4609	01:04

As set 1, the fitted data at the pressure of 1350.0000-1950.0000 mmHg (when $\frac{p}{p_0}$ is in the range from0.051 to 0.075 and in the required range of the BET formula) is shown in the following graph and tables.

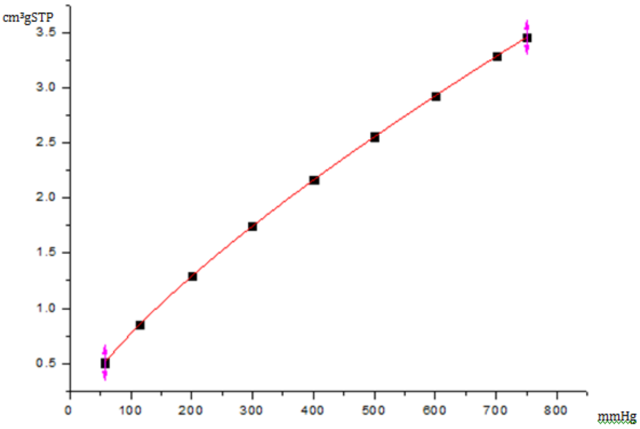
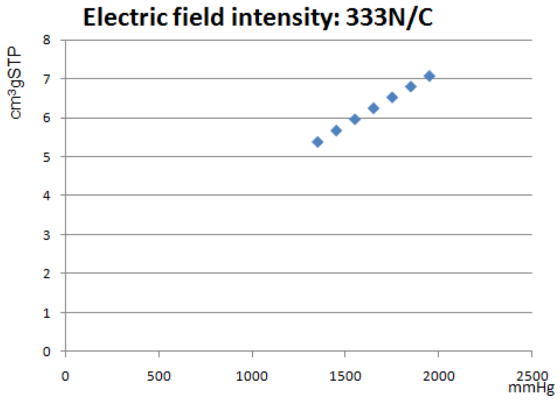


Fig.3.3-6 Original data and fitting result(333N/C)

$q = kp^{\frac{1}{n}}$		
	Value	Standard Error
k	0.02479	3.15881×10^{-5}
n	1.34049	3.68539×10^{-4}

Absolute Pressure(mmHg)	Quantity Adsorbed (cm^3g STP)	$\frac{p}{p_0}$	$\frac{V}{V_1}$
1350.0000	5.363832	0.051645	0.892372163
1450.0000	5.657524	0.055471	0.892558864
1550.0000	5.946111	0.059297	0.892733144
1650.0000	6.230004	0.063122	0.892896555
1750.0000	6.509557	0.066948	0.893050375
1850.0000	6.785080	0.070773	0.893195669
1950.0000	7.056843	0.074599	0.893333335

The data is fitted into the model $\frac{V}{V_1}=\frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$, where $x=\frac{p}{p_0}$. Let $y=\frac{V}{V_1}$ and $d=e^{\alpha E_m^4+\beta E_m^2}$ as the electric field intensity is a constant. The fitting result is shown in the following graphs and tables.



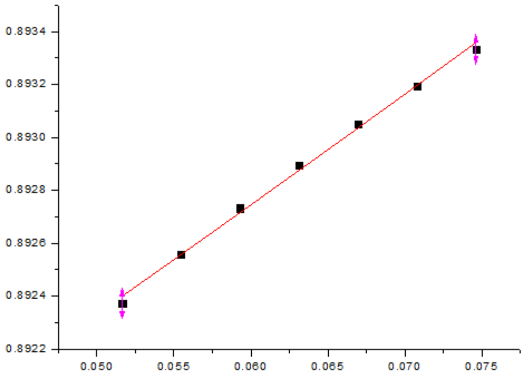


Fig.3.3-7 Calculated value of adsorption capacity(333N/C)

Fig.3.3-8 Fitting result of calculated value(333N/C)

$y=\frac{1-x+cdx}{d(1-x)+cdx}$		
	Value	Standard Error
c	0.35028	0.00921
d	1.12316	8.49093×10^{-5}

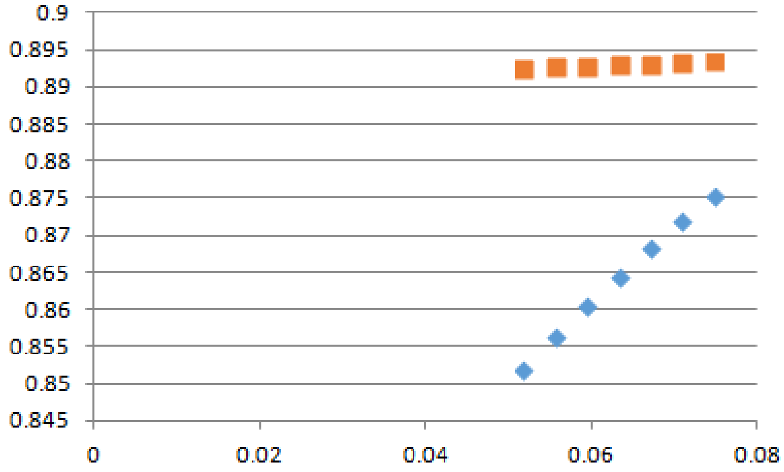
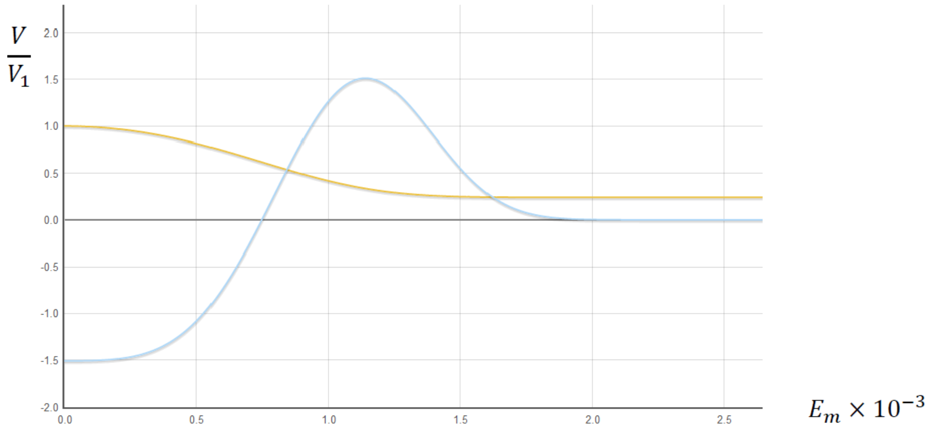


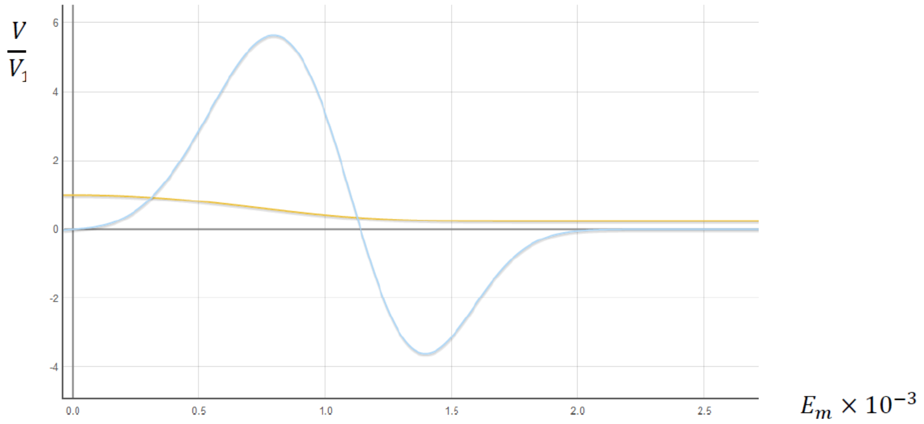
Fig.3.3-9 Comparison between adsorption capacity under 500N/C(blue) and333N/C(orange)

Combine three series of data together, substitute it into the equation $\frac{V}{V_1}=\frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$, and figure out$\alpha=4.61668\times 10^{-13}$, $\beta=9.94019\times$

10^{-7} . Take $x = \frac{p}{p_0} = 0.05,$. Considering the electric field intensity range in the experiment, take the approximation $C = \frac{C_1+C_2}{2} = 6.03325$. Take the second and third derivative of the function $f(E_m) = \frac{V}{V_1} = \frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$. The graph of primitive function and its second derivative is shown below:



The graph of primitive function and its third derivative is shown below:



Solve the equation $f'''(E_m) = 0$, and the solutions are $E_{m1} = 0.00\mathrm{N/C}$ and $E_{m2} = 1140.30\mathrm{N/C}$. Therefore, the electric field intensity interval in which the adsorption capacity changes significantly with electric field intensity is $[0.00\mathrm{N/C}, 1140.30\mathrm{N/C}]$.

3.4 Conclusions

The following conclusions can be drawn after three sets of experiment:

(1) At given temperature, the effect of electric field intensity and pressure on the

adsorption capacity of CO_2 on silica aerogel accords with the equation $\frac{V}{V_1} = \frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$, where $\alpha = 4.61668 \times 10^{-13}$, $\beta = 9.94019 \times 10^{-7}$. The experiment results were consistent with the function images and we can draw the conclusion from the graph that the adsorption capacity can increase by 400% most in electric field

(2) In the adsorption process of CO_2 on the aerogel, with the parameters α andβ, it is figured out that the electric field intensity interval in which the adsorption capacity changes significantly is $[0.00\mathrm{N/C}, 1140.30\mathrm{N/C}]$.

4. Conclusions and prospects

4.1 Conclusions

(1)In a certain pressure interval, the adsorption capacity of CO_2 on silica aerogelper unit mass is affected significantly by the electric field. The adsorption capacity of CO_2 increases with electric field intensity at a given pressure. Based on the BET theory, the adsorption process can be well described by the equation$\frac{V}{V_1}=\frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$. In certain conditions, compared with the adsorption process without electric field, the adsorption capacity can increase by 400% most in electric field. The isotherm of adsorption in electric field has almost the same shape as adsorption without electric field, while it moves upwards on the whole.

(2)At certain temperature, how adsorption capacity changes with electric field intensity and pressure can be described by the equation $\frac{V}{V_1}=\frac{(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}{e^{\alpha E_m^4+\beta E_m^2}(1-x)+Ce^{\alpha E_m^4+\beta E_m^2}x}$. At certain pressure, how adsorption capacity changes with electric field intensity and temperature can be described by $\frac{V}{V_1}=\frac{(1-x)+Ce^{(A_1E_m^4+B_1E_m^2)/T}x}{e^{(A_1E_m^4+B_1E_m^2)/T}(1-x)+Ce^{(A_1E_m^4+B_1E_m^2)/T}x}$.

(3) The interval in which the adsorption of $\mathrm{CO_2}$on silica aerogel changes with electric field intensity significantly is $[0.00\mathrm{N/C}, 1140.30\mathrm{N/C}]$.The interval is different for different gases. Therefore, selective adsorption is achievable by controlling the electric field intensity.

4.2Applications and future prospects

(1)In the thesis, by studying the effect of electric field on adsorption of CO_2 on silica aerogel, it is known that the adsorption capacity of gases likeCO_2, NO_2 andSO_2on aerogel or other porous materials per unit mass can be increased by adding an external electric field. Therefore, the use of porous materials becomes more efficient. The method can be further applied to the producing filtrating equipment of automobile exhausts, controlling industrial waste, or collecting greenhouse gases like CO_2, which reduces the emission of harmful and greenhouse gases.

(2) Based on the conclusions, the further conjecture is that on a certain kind of material, the interval of electric field intensity in which the adsorption capacity changes most with the electric field is different for different non-polar gases. As electric field has different effect on the intermolecular potential energy of different gas molecules, the interval is supposed to vary with the types of gases, which shows the possibility to make selective adsorption of mixed gases by changing electric field intensity. However, the porous structure of materials is idealized in the research. Further analysis of porosity and surface area should be adopted in the research of next stage. The conjecture should be confirmed quantitatively through future studies into adsorption of other non-polar gases, and the idea can be of great value in gas separation in chemical industry. In addition, adsorption of polar gases can be one of the future directions.

(3)As it requires simple equipment and low electricity power to add electric field, compared to the ways of cooling or pressurization, which ask for strict condition in a closed system, it turns out to be more efficient and energy-saving to make the adsorption process in electric field. In spite of the energy loss during the electric power transmission and work applying process to gas molecules, a small amount of electric power is enough to apply electric field and make effect on adsorption capacity and selective adsorption ability.

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