

# Experimental Evaluation of Adsorption Kinetics of Activated Carbon/HFC-134a Pair

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This article deals with the experimental evaluation of adsorption kinetics of HFC-134a on highly porous activated carbon of type Maxsorb III by constant volume variable pressure (CVVP) method over a temperature ranging from 20 to 60°C. These data are useful for the operation of adsorption chillers and these data are unavailable in the literature. Data obtained from the kinetic studies were treated according to the various kinetic models with the Fickian diffusion model being the most suitable overall. Guided by the experimental measurements, the surface diffusion is also estimated and is found that it follows the classical Arrhenius law within the experimental range.

**Key words:** *Adsorption kinetics, Maxsorb III, HFC-134a, CVVP*

## 1. Introduction

The physical adsorption process occurs mainly within the pores and surface of the adsorbent. It requires the knowledge of adsorption characteristics when the temperatures and pressures are varying. In the fields of adsorption cooling<sup>1-2)</sup>, purification of gas<sup>3-4)</sup>, separation process<sup>5-6)</sup>, natural gas storage<sup>7-8)</sup>, adsorption on a solid adsorbent is a fundamental process. Generally, the thermo-physical properties (surface area, pore volume, particle diameter etc.) of an adsorbent play a vital role in the adsorption characteristics of adsorbent-refrigerant pair. Pitched based activated carbon (type Maxsorb III) can become a potential adsorbent in the field of refrigeration because some studies in Maxsorb III have already been made<sup>9-10)</sup>. Comparing with the palletized or granular activated carbon; Maxsorb III has many intrinsic characteristics that are superior to them. For example, Maxsorb III has large surface area and fast inter-particle adsorption kinetics<sup>9)</sup>.

In order to develop adsorption based systems, it is inevitable to determine adsorption isotherms, kinetics of the assorted adsorbent-refrigerant pair. It is essential to estimate the kinetics of adsorbent-refrigerant

pair accurately for design purposes and improving understanding of chillers. Design codes of the chiller must be equipped with the correct isotherms, isosteric heat of adsorption and the coefficients of uptake model. With these key data available, only then the numerical modeling of the processes of the chiller operation can be estimated accurately with a high level of confidence<sup>10)</sup>.

In this article, adsorption rate of HFC-134a on Maxsorb III specimen has been experimentally measured by constant volume variable pressure (CVVP) method when the temperatures are varying from 20 to 60°C. To analyze the experimental data, the Fickian diffusion model is used and found to be fairly matched within the acceptable experimental uncertainties.

## 2. Experimental

### 2.1 Materials

The pitch based activated carbon (Maxsorb III specimen) labeled as MSC-30 has been supplied by the Kansai Coke and Chemical Co. Ltd., Japan. It has a Brunauer-Emmet-Teller (BET) surface area of 3,140 m<sup>2</sup>/g and micropore volume of 1.7 cc/g. The mean particle diameter of Maxsorb-III specimen is 72 μm, ash content is less than

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0.1%, moisture of no more than 0.8% and pH value is 4.1.

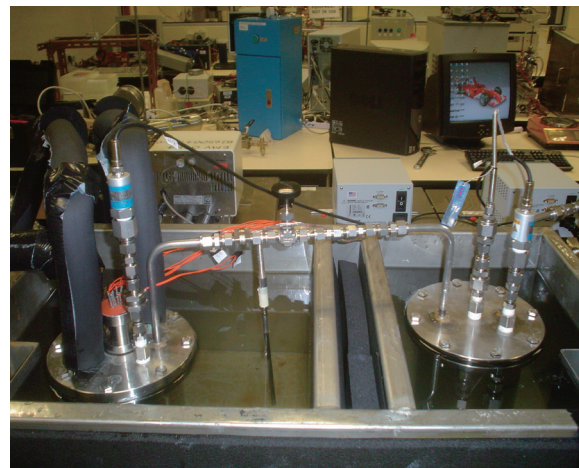
## 2.2 Experimental setup

Figure 1 and 2 show the photograph and schematic diagram of the experimental test rig, respectively. The experimental setup comprises (i) a charging tank made of stainless steel (SS 304) with a volume of 2570 cc whose volume was inclusive of related piping and valves, (ii) an adsorption tank made of stainless steel (SS 304) with a volume of 2427 cc, whose volume was again inclusive of related piping and valves, (iii) two constant temperature baths of model HAAKE-F8-C35 and Polyscience on which the both the charging and adsorption tanks are immersed to control the temperatures of both charging and adsorption tanks, (iv) a KYOWA PGA-10KA pressure transducer with an uncertainty of 0.1% of full scale and a pressure range of 0-1 MPa, (v) Class-A type Pt 100  $\Omega$  resistance temperature detector (diameter = 1/16 inch) with an uncertainty of  $\pm 0.1$  K for temperature measurement, (vi) four thermistors (Model: Omega 4407) with a resistance of 5000  $\Omega$  at 25°C with an uncertainty of  $\pm 0.2$ °C and maximum operating temperature of 150°C connected with the activated carbon for direct temperature measurement, (vii) a vacuum pump a BOC Edwards direct drive vane vacuum pump to a vacuum level of 0.05 mbar, and (viii) Agilent data logger to record the data. Three filters (diameter = 5  $\mu$ m) that are capable of stopping migration of activated carbon particles during evacuation and desorption were fitted at three different exits of the adsorption tank.

## 2.3 Experimental procedure

Prior to experiment, the entire test rig is evacuated for 24 hours using a BOC Edwards direct drive vane vacuum pump to a vacuum level of 0.05 mbar. During the evacuation, the test system is regenerated in situ 120-130 °C for 12 h to desorb any residue gas in the system. At the end of regeneration process, the test system is purged with helium gas with a purity of 99.9995% and evacuated further to achieve low vacuum conditions. The evacuation and helium purging is continued several times to ensure that there is no residual gas left in the system. Based on the measurements, there is no measurable interaction between the inert gas and the

adsorbent, as the effect if the partial pressure of helium in the tanks is found to be small. After evacuation, the charging cell is pressurized with the assorted refrigerant and left to reach an equilibrium state (with the ball valve closed). During charging, it is necessary that the charging pressure should be less than the saturation pressure of the refrigerant at that temperature to ensure no condensation is occurred. At this state the initial pressure and temperature in the charging cell are measured before adsorption. Once equilibrium is achieved, the ball valve between the charging and adsorption tank is opened. The pressure and temperature in the adsorption tank are recorded. With the known initial mass of dry Maxsorb III, the temperature of the test system is varied to calculate uptake of the assorted refrigerant varying with time.



**Fig. 1** Photograph of the experimental test rig.

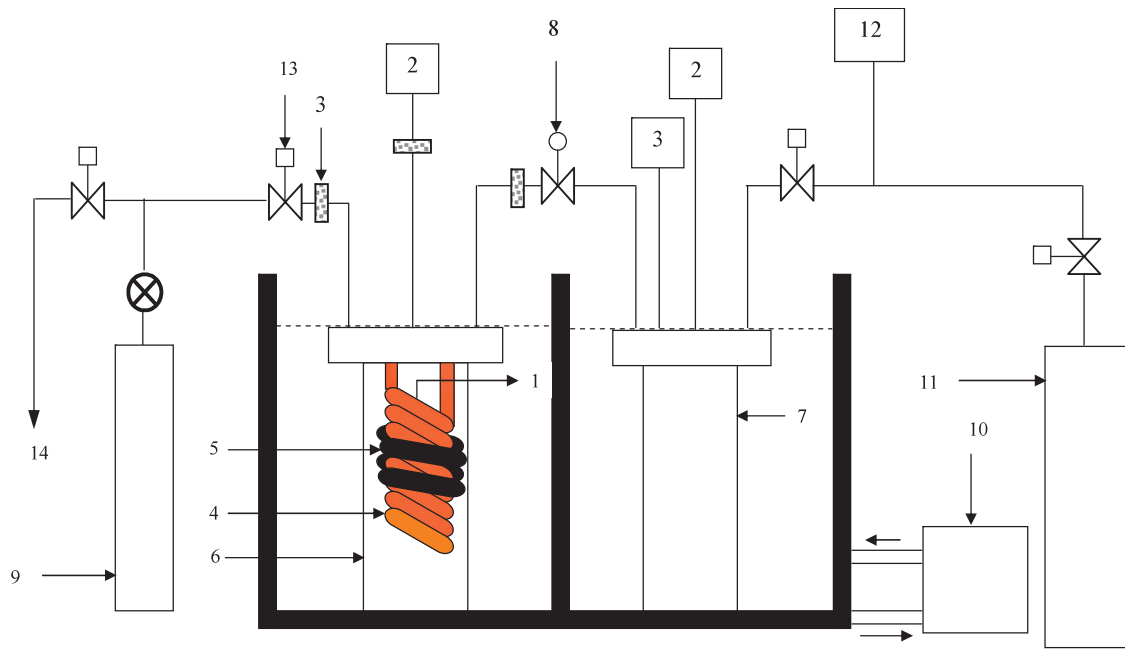
## 3. Mathematical modeling

### 3.1 Semi-infinite model

I.I. El-Sharkawy et al.<sup>11)</sup> reported that during the initial phase of adsorption surface diffusion coefficient follows the uptake behavior of semi-infinite medium of any particle shape and is expressed by,

$$\frac{C}{C_0} = \frac{2A}{V} \left( \frac{D_s t}{\pi} \right)^{\frac{1}{2}} \quad (1)$$

where  $A$  is the area of the adsorbent particle,  $V$  represents particle volume and  $D_s$  stands



1: Thermistor; 2: Pressure transducer; 3: Filter; 4: Copper coil; 5: Activated carbon; 6: Adsorption tank; 7: Charging tank; 8: Needle valve; 9: Helium gas cylinder; 10: Water circulator; 11: Refrigerant cylinder; 12: Pressure regulator; 13: Ball valve and 14: To vacuum pump

**Fig. 2** Schematic diagram of the experimental test rig.

for surface diffusion. Maxsorb III samples have been assumed to be spherical.

A plot of the relative uptake and square root of time for each isotherm yields with a slope of

$$\frac{2A}{V} \sqrt{\frac{D_s}{\pi}}$$

Surface diffusion,  $D_s$  can be expressed as,

$$D_s = D_{so} \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

Eq. (2) can be re-arranged as,

$$\ln(D_s) = -\frac{E_a}{R} \frac{1}{T} + \ln(D_{so}) \quad (3)$$

By plotting  $\ln(D_s)$  against  $1/T$ , one can get the numerical values of activation energy,  $E_a$  and the pre-exponential coefficient,  $D_{so}$ . This plot

is popularly known as Arrhenius plot. There exists a linear relationship between  $\ln(D_s)$  and  $1/T$ . The slope yields  $-E_a/R$  and the intercept provide the pre-exponential constant,  $D_{so}$  from eq. (3).

The Fickian diffusion model is used to evaluate adsorption kinetics of various types of adsorbate pairs. The Fickian model is valid when the diffusivity is independent of sorbate concentration when the system is thermodynamically ideal<sup>11)</sup>. The diffusion equation is used to express adsorption rate in spherical shaped adsorbent,

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_s \frac{\partial C}{\partial r} \right) \quad (4)$$

$C$  is the adsorbate concentration,  $D_s$  is the diffusion coefficient;  $r$  is the radial coordinate. Considering a constant diffusivity and applying the appropriate initial and boundary conditions, the eq. (4) can be written as<sup>11)</sup>,

$$\frac{C}{C_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_s t}{R_p^2}\right) \quad (5)$$

where  $n$  is an integer from 1 to infinity,  $R_p$  is the radius of the particles and  $C_0$  stands for limiting uptake and can be estimated from the following equation.

$$C_0 = (\text{BET surface area of Maxsorb III})/a_0$$

where  $a_0$  is the molecular area of adsorbate and is calculated by<sup>12)</sup>,

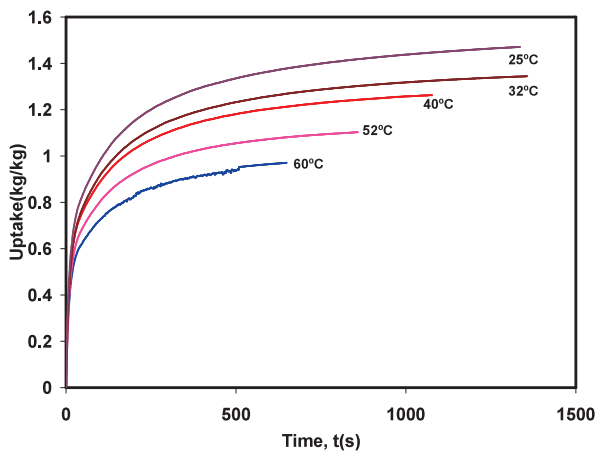
$$a_0 = 1.091 \left( \frac{M}{\rho_{lb} N_A} \right)^{\frac{2}{3}} \quad (6)$$

where,  $M$  is the molecular weight of adsorbate,  $\rho_{lb}$  is the density of liquid phase of adsorbate at boiling point temperature in  $\text{g}/\text{cm}^3$ . Surface area of adsorbate can be calculated as<sup>12)</sup>,

$$A_0 = N_A a_0 \quad (7)$$

## 4. Results and Discussion

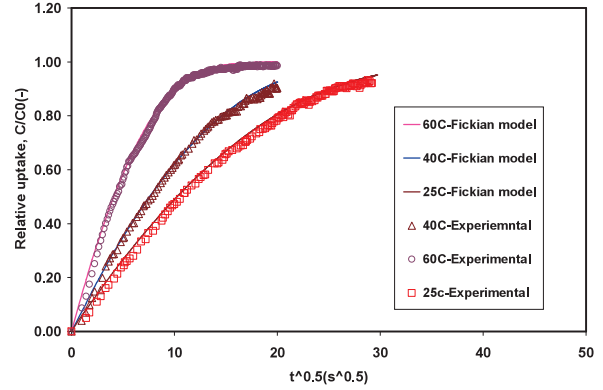
Fig. 3 shows the kinetic uptake of HFC-134a on Maxsorb III when temperatures are varying from 20 to 60°C. It is observable from Fig. 3 that when the adsorption temperature is 25°C, the Maxsorb III can adsorb R134a as high as 1.5 kg/kg within an adsorption time interval of 1400s. However, when the adsorption temperature is 60°C, only 600 s is required to achieve equilibrium uptake of 0.85 kg/kg.



**Fig. 3** Kinetic uptake of HFC-134a on Maxsorb III at various temperatures.

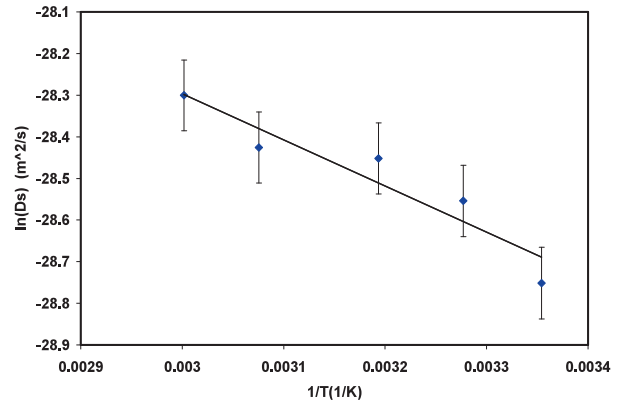
Fig. 4 depicts plots of relative uptake vs square root of time for Maxsorb III/R134a pair. It is observable from Fig. 4 that solid

lines represent the fitting of eq.(5) where the diffusion time constant is calculated assuming semi-infinite model. It is also noticeable from Fig. 4 that an accurate estimation of relative uptake can be evaluated using the Fickian diffusion model which indicates the goodness of fit.



**Fig.4** Relative uptake vs square root of time.

A linear relationship between  $\ln(D_s)$  and  $1/T$  is observed in Fig. 5. It is also visible from Fig. 5 that the diffusivity of Maxsorb III increases with the adsorption temperature which ultimately agrees well with the Arrhenius trend.



**Fig. 5** Plot of  $\ln(D_s)$  vs  $1/T$ .

## 4. Conclusions

Adsorption rate of HFC-134a on Maxsorb III has been evaluated by CVVP method over a wide range of temperatures of 20 to 60°C. The Fickian diffusion model is used to analyze the experimental data and are found to be fairly consistent within the acceptable

uncertainties. The present kinetics data of HFC-134a are useful in designing adsorption chiller.

### Nomenclature

$C$	adsorption uptake	kg/kg
$C_0$	limiting adsorption uptake	kg/kg
$A$	area of particle	$m^2$
$V$	volume of particle	$m^3$
$D_s$	surface diffusion	$m^2/s$
$t$	time	s
$r$	radial coordinate	m
$E_a$	activation energy	J/kg
$D_{s0}$	pre-exponential coefficient	-
$M$	molecular weight	kg/kmol
$a_0$	surface area of adsorbate of 1 molecule	$m^2$
$A$	surface area of adsorbate	$m^2$
$N_A$	Avogadro's number	-

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