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**Azahar, Fatin Hazwani M.**

Kyushu University Program for Leading Graduate School, Green Asia Education Center,  
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University |  
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

**Yabushita, Akihiro**

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

**Harata, Akira**

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

**Saha, Bidyut Baran**

International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University |  
Mechanical Engineering Department, Kyushu University

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## Study on the Isotheric Heat and Its Effect on the Adsorption Systems for Various Sorption Pairs

Fatin Hazwani M. Azahar<sup>1,2</sup>, Akihiro Yabushita<sup>2</sup>, Akira Harata<sup>2\*</sup>, Bidyut Baran Saha<sup>3,4</sup>, Kyaw Thu<sup>1,2\*</sup>

<sup>1</sup> Kyushu University Program for Leading Graduate School, Green Asia Education Center, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga-koen 6-1, Kasuga-shi, Fukuoka 816-8580, Japan

<sup>2</sup> Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga-koen 6-1, Kasuga-shi, Fukuoka 816-8580, Japan

<sup>3</sup> International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

<sup>4</sup> Mechanical Engineering Department, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

**Abstract:** *This paper presents the theoretical frameworks of isotheric heat of adsorption for sub-critical adsorption phenomena. The contribution by the adsorbed phase on the isotheric heat at different relative pressure is accounted for. The isotheric heat of several adsorption pairs namely Water + Silica Gel, Propane + highly porous activated carbon type Maxsorb III, and Ethanol + spherical phenol resin treated with different mass ratios of KOH named as KOH6-PR, were evaluated using improved isotherm fitting with higher accuracy. Dubinin-Astakhov isotherm is employed to fit the isotherm data and the results were compared between such adsorbate/adsorbent pairs. Relatively lower values of isotheric heat at low coverage were observed and the effect of the isotheric heat at various coverages on the theoretical performance (COP) of the adsorption systems is also reported.*

**Keywords:** Isotheric Heat, Isotherm, Maxsorb III, Adsorption

### 1. INTRODUCTION

In adsorption process, the adsorbate molecules tend to experience phase changes from the gaseous phase to the adsorbed phase due to van der Waals forces, where the reduction in the energy level between these phases occurs due to the release of kinetic energy [1]. Thus, adsorption process is an exothermic process where the adsorbed phase is not only function of pressure and temperature, but the it is also a function of uptake or mass of adsorbent [2]. The associated released heat during the adsorption process is normally termed as an isotheric heat which can be defined as the enthalpy changes in the adsorbent+adsorbate system with respect to the adsorbed amount changes at constant pressure, temperature and mass of adsorbent (Eq.1) [2]. Thus, the isotheric heat is a very important parameter in adsorption thermodynamics and system design. The isotheric heat is often evaluated using the Clausius-Clayperon equation where the adsorbate molecules are assumed to behave as ideal gas. Moreover, the accurate isotheric heat is crucial in the adsorption cooling and heating applications as it contributes to the raise in temperature in adsorption beds [3].

This paper describes the thermodynamic quantities by theoretical frameworks namely the isotheric heat, entropy, and specific heat capacity employing the adsorption thermodynamics. In this study, three commonly used adsorbent+adsorbate pairs namely; (1) Silica gel+water, (2) Maxsorb III+ethanol and (3) Maxsorb III+Propane, were selected for temperatures ranging from 278 K to 348 K. The properties of the adsorbates were evaluated using the Reference Fluid Thermodynamic and Transport Properties database of NIST (REFPROP). The adsorption uptakes data for these pairs were taken from the published experimental

work [5], [6], [7]. These data were fitted using the Dubinin-Astakhov (D-A) isotherm equation where the parameters such as the characteristic energy, surface heterogeneity parameter and the limiting uptake were regressed using Generalized Reduced Gradient method. The isotheric heat of the studied pairs were then estimated by employing the D-A equation. The efficacy of adsorption cycles using the selected pairs is evaluated using the theoretical coefficient of performance at assorted uptakes.

### 2. ADSORPTION THERMODYNAMICS

The adsorption systems such as adsorption chillers, refrigeration system, dehumidification and desalination, associate with the physisorption. The physisorption process of an adsorbate onto both micro- and macroporous surfaces of an adsorbent occurs when the adsorbed phase is held near to the pores by weak intermolecular forces such as van der Waals forces [4]. For fully describing thermodynamic state of this system, it is necessary to have three characteristic balances such as (i) heat (Q), (ii) mass of the adsorbate in the adsorbed phase ( $m_a$ ), mass of molecules in gaseous phase ( $m_g$ ), and (iv) chemical potential in adsorbed phase ( $\mu_a$ ) and gaseous phase ( $\mu_g$ ). All of the extensive properties for the expression of isotheric heat are described as the function of pressure (P), temperature (T) and uptake (x) and is given by,

$$Q_{st} = \left( \frac{\partial Q}{\partial m_a} \right)_{P,T,M_s} \quad (1)$$

## 2.1 Derivation of Total Differential Physisorption Extensive Property (Entropy)

Since in the adsorbent-adsorbate system consists of solid and adsorbed phase, total differential of entropy is the summation of these two phases where,

$$ds = ds_s + ds_a \quad (2)$$

The subscript s and a describe the solid phase and adsorbed phase, respectively. The entropy of the adsorbent as a function of P and T is given as,

$$ds_s = \left( \frac{\partial S_s}{\partial T} \right)_P dT + \left( \frac{\partial S_s}{\partial P} \right)_T dP = \frac{c_{p,s}}{T} dT - \left( \frac{\partial v_s}{\partial T} \right)_P dP \quad (3)$$

Similarly, in the adsorbed phase,

$$ds_a = \left( \frac{\partial S_a}{\partial T} \right)_{P,x} dT + \left( \frac{\partial S_a}{\partial P} \right)_{T,x} dP + \left( \frac{\partial S_a}{\partial x} \right)_{P,T} dx \quad (4)$$

where the first term denotes the change in entropy with respect to temperature at constant pressure and the amount of uptake, the second term refers to the change in entropy as a function of pressure at constant temperature and adsorbate uptake, and the last term represents the change in entropy with respect to the amount of adsorbate uptake. From Maxwell relationship, the first and second term can be written as;

$$\left( \frac{\partial S_a}{\partial T} \right)_{P,x} \approx c_{p,a} / T \quad (5)$$

$$\left( \frac{\partial S_a}{\partial P} \right)_{T,x} = - \left( \frac{\partial v_a}{\partial T} \right)_{P,x} \quad (6)$$

## 2.2 The Partial Entropy of Adsorption $(\partial S_a / \partial x)_{P,T}$

It should be noted that the Gibbs free energy (G) contributes to the differential form in the adsorbed phase and is given by;

$$dG_a = -S_a dT + V_a dP + \mu_a dm_a \quad (7)$$

The chemical potential of adsorbed phase is defined as the partial change in internal energy (u) with respect to the adsorbate uptake (x). Therefore, the total chemical potential in both adsorbed and gaseous phase is given by;

$$\mu_a = \left[ \left( \frac{\partial u}{\partial P} \right)_{s,v,\mu_g} \right]$$

$$d\mu_a = - \left( \frac{\partial S_a}{\partial x} \right)_{T,P} dT + \left( \frac{\partial v_a}{\partial x} \right)_{T,P} dP + \left( \frac{\partial \mu_a}{\partial x} \right)_{T,P} dx \quad (8)$$

$$d\mu_g = -s_g dT + v_g dP \quad (9)$$

At equilibrium, the chemical potential in adsorbed phase is equal to that in gaseous phase, and can be written as;

$$\mu_a = \mu_g$$

$$d\mu_a = d\mu_g$$

$$\left( \frac{\partial S_a}{\partial x} \right)_{T,P} dT + \left( \frac{\partial v_a}{\partial x} \right)_{T,P} dP - \left( \frac{\partial \mu_a}{\partial x} \right)_{T,P} dx = s_g dT + v_g dP \quad (10)$$

However, at constant amount of adsorbate,

$$\left( \frac{\partial \mu_a}{\partial x} \right)_{T,P} = 0$$

$$\left( \frac{\partial S_a}{\partial x} \right)_{T,P} dT = s_g dT + v_g dP + \left( \frac{\partial v_a}{\partial x} \right)_{T,P} dP$$

$$\left( \frac{\partial S_a}{\partial x} \right)_{T,P} = s_g - v_g \frac{dP}{dT} + v_a \frac{dP}{dT}$$

$$\left( \frac{\partial S_a}{\partial x} \right)_{T,P} = s_g - (v_g - v_a) \frac{dP}{dT} \quad (11)$$

Lastly, the total differential entropy of an adsorbate-adsorbent system can be expressed as;

$$ds = \left( \frac{c_{p,s}}{T} + \frac{c_{p,a}}{T} \right) dT - \left( \frac{\partial v_a}{\partial T} \right)_P dP - \left( \frac{\partial v_a}{\partial T} \right)_{P,x} dP + \left\{ s_g - (v_g - v_a) \frac{dP}{dT} \right\} dx \quad (12)$$

## 2.3 Expression of Isotheric Heat by Clausius-Clayperon

It is well known that two assumptions were made in the Clausius-Clayperon (C-C) equation, (i) the bulk gas phase is considered as ideal and (ii) the volume in adsorbed phase is neglected. However, these assumptions are only true for low pressure and might not be applicable at higher pressures [4].

The integral change in isotheric heat is expressed as

$$-dq = Tds \quad (13)$$

Where s refers to the summation of total entropies in gaseous, adsorbed and solid phases.

$$S = S_g + S_s + S_a$$

$$Q_{st} = -T \left( \frac{\partial \{S_g + S_a + S_s\}}{\partial m_a} \right)_{P,T,M_s}$$

$$= -T \left[ \left( \frac{\partial S_g}{\partial m_a} \right)_{P,T,M_s} + \left( \frac{\partial S_a}{\partial m_a} \right)_{P,T,M_s} + \left( \frac{\partial S_s}{\partial m_a} \right)_{P,T,M_s} \right] \quad (14)$$

Ignoring the entropy change of the adsorbent (s), we have  $\left( \frac{\partial S_s}{\partial m_a} \right)_{P,T,M_s} \approx 0$ .

Mass balance:

$$dm_a = -dm_g$$

$$Q_{st} = -T \left[ \left( \frac{\partial S_a}{\partial m_a} \right)_{P,T,M_s} - \left( \frac{\partial S_g}{\partial m_g} \right)_{P,T,M_s} \right] \quad (15)$$

$$\begin{aligned} & - \left( \frac{\partial s_a}{\partial m_a} \right)_{T,P} dT + \left( \frac{\partial v_a}{\partial m_a} \right)_{T,P} dP \\ & = - \left( \frac{\partial s_g}{\partial m_g} \right)_{T,P} dT + \left( \frac{\partial v_g}{\partial m_g} \right)_{T,P} dP \left( \frac{\partial S_a}{\partial m_a} \right)_{T,P} - \left( \frac{\partial S_g}{\partial m_g} \right)_{T,P} \\ Q_{st} & = - \left[ \left( \frac{\partial v_g}{\partial m_g} \right)_{T,P} - \left( \frac{\partial v_a}{\partial m_a} \right)_{T,P} \right] \frac{dP}{dT} \end{aligned} \quad (16)$$

Finally, isosteric heat reduces to:

$$\begin{aligned} Q_{st} & = T \left[ \left( \frac{\partial v_g}{\partial m_g} \right)_{T,P} - \left( \frac{\partial v_a}{\partial m_a} \right)_{T,P} \right] \frac{dP}{dT} \\ Q_{st} & = T(v_g - v_a) \frac{dP}{dT} \end{aligned} \quad (17)$$

Since the pressure in adsorbed phase is in the function of T and  $m_a$ ,  $P=P(T,m_a)$ , the pressure gradient with the temperature during adsorption process is expressed by;

$$\frac{dP}{dT} = \left( \frac{\partial P}{\partial m_a} \right)_T \frac{dm_a}{dT} + \left( \frac{\partial P}{\partial T} \right)_{m_a} \quad (18)$$

By neglecting the volume in adsorbed phase, the expression of isosteric heat becomes;

$$\begin{aligned} Q_{st} & = RT^2 \left( \frac{\partial \ln P}{\partial T} \right)_{m_a} + T v_g \left( \frac{\partial P}{\partial m_a} \right)_T \frac{dm_a}{dT} \\ & \approx RT^2 \left( \frac{\partial \ln P}{\partial T} \right)_{m_a} + T v_g \left( \frac{\partial P}{\partial T} \right)_{gas} \end{aligned} \quad (19)$$

Where the first term represents the Clausius-Clayperon form and the second term refers to the occurrence of the non-ideality in the gaseous phase.

### 3. RESULT AND DISCUSSION

#### 3.1 Adsorption Parameters

The Dubinin-Astakhov (D-A) (Eq. 20) model is found to provide the best fitting for isotherm data for the selected pairs. The D-A equation can be expressed as;

$$x = x_m \text{Exp} \left( - \left( \frac{RT}{E} \ln \frac{P_s}{P} \right)^n \right). \quad (20)$$

Where x is the instantaneous uptake,  $x_m$  is the limiting uptake, R is the gas constant, T is the adsorption temperature, n is the surface heterogeneity, E refers to

the characteristic energy,  $P_s$  and P is the saturation and evaporator pressure respectively.

Similarly, the expression of D-A model in terms of pressure can be written as;

$$\ln P = \ln P_s - \frac{E}{RT} (-\ln \theta)^{1/n} \quad (21)$$

where  $\theta$  is the uptake amount referring to  $\frac{x}{x_m}$ .

From the derivation of isosteric heat using Clausius-Clayperon relation, Chakraborty et. al [2] derived the equation of isosteric heat employing D-A equation;

$$\begin{aligned} dP & = \frac{\partial P}{\partial T} \Big|_x dT + \frac{\partial P}{\partial x} \Big|_T dx \\ \frac{dP}{dT} & = \frac{\partial P}{\partial T} \Big|_x + \frac{\partial P}{\partial x} \Big|_T \frac{dx}{dT} \end{aligned} \quad (22)$$

Using eq. (20) and (21),

$$\begin{aligned} \frac{\partial \ln P}{\partial T} \Big|_x & = \frac{\partial \ln P_s}{\partial T} \Big|_x + \frac{E}{RT^2} (-\ln \theta)^{1/n} \\ & = \frac{h_{fg}}{RT^2} + \frac{E}{RT^2} (-\ln \theta)^{1/n} \\ \frac{dP}{dT} & = \frac{P}{RT^2} [h_{fg} + E(-\ln \theta)^{1/n}] + \frac{\partial P}{\partial x} \Big|_T \frac{dx}{dT} \end{aligned} \quad (23)$$

Hence, the isosteric heat of adsorption reduces,

$$\begin{aligned} Q_{st} & = T v_g \frac{dP}{dT} = \frac{T^2 R}{P} \frac{dP}{dT} \\ Q_{st} & = h_{fg} + E(-\ln \theta)^{1/n} + T v_g \frac{\partial P}{\partial x} \Big|_T \frac{dx}{dT} \end{aligned} \quad (24)$$

Figs. 1a, 1b and 1c show the adsorption uptake data of silica gel+water, KOH6-PR+ethanol, and Maxsorb III+propane at temperatures ranging from 5°C to 75°C, regressed with the D-A isotherm model. It can be clearly seen that for one kg of different adsorbent, it gives different uptake value depending on the adsorbate paired to it. Numerical regressed isotherms are furnished in Table 2.

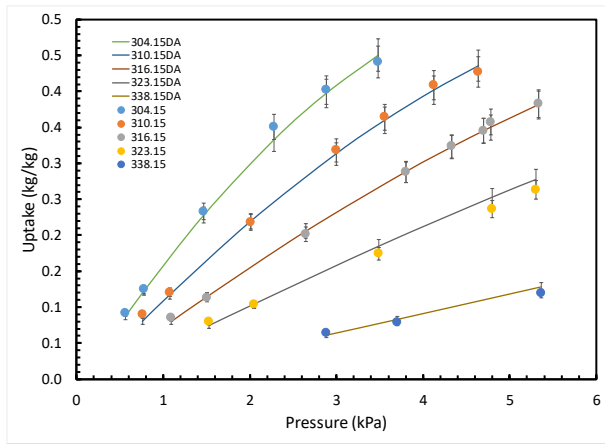


Fig. 1a. Adsorption isotherm of silica gel+water pair fitted with D-A model.

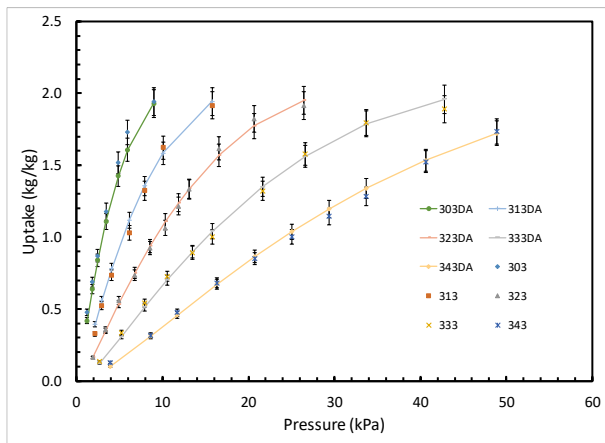


Fig. 1b. Adsorption isotherm of KOH6-PR+ethanol pair fitted with D-A model.

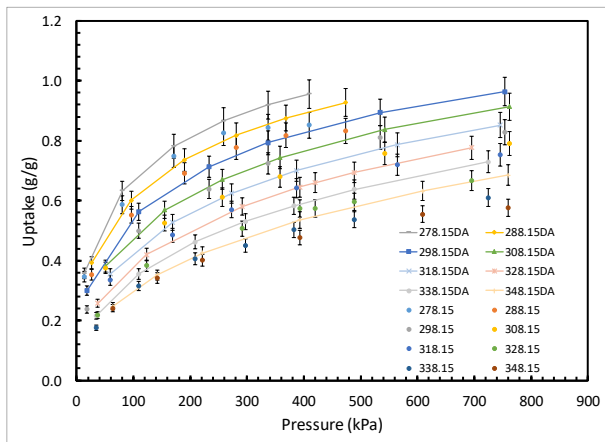


Fig. 1c. Adsorption isotherm of Maxsorb III+propane pair fitted with D-A model.

**Table 2**

Isotherm parameters of KOH6-PR+ethanol, silica gel+water and Maxsorb III+propane.

Material	$W_0$ [kg kg <sup>-1</sup> ]	$n$ [-]	$E$ [J mol <sup>-1</sup> ]
KOH6-PR+ethanol	1.9843	1.4973	3997.514
Silica gel+water	0.50881	1.2753	3363.50
Maxsorb III+propane	0.89949	1.2373	8382.805

### 3.2 Isothermic Heat of Adsorption

The isothermic heat of adsorption is estimated using Eq.

(24) and the result of  $Q_{st}$  against adsorbate loading for silica gel+water, KOH6-PR+ethanol, Maxsorb III+propane pairs are plotted in Figs. 2a, 2b and 2c, respectively. The figures proved that the isosteric heat decreases with the increase of adsorption uptake and temperature, where it proves Eq. (1) that the heat of adsorption is a function of pressure (P), temperature (T) and mass of adsorbent ( $M_s$ ). As the heat of vaporization ( $h_{fg}$ ) decreases with temperature, the isosteric heat also decreases with temperature. The comparison of these three adsorbent-adsorbate pairs shows that Maxsorb III+propane offers the lowest isosteric heat. For silica gel+water pair, the isosteric heat shows relatively higher value as compared to both KOH6-PR+ethanol and Maxsorb III+propane pairs. This may be due to the micro and meso-porous structures combination in silica gel.

### 3.3 Coefficient of Performance (COP)

The theoretical coefficient of performance for an adsorptive system is usually estimated using Eq. (25) as below,

$$COP = \frac{h_{fg}}{Q_{st}} \quad (25)$$

where  $h_{fg}$  refers to the specific enthalpy change of vaporization ( $h_g-h_f$ ), and  $Q_{st}$  represents isosteric heat which its value can be obtained from Eq. (24). Figure 3 shows the coefficient of performance versus adsorbate loading plot for the three pairs, i.e., silica gel+water, KOH6-PR+ethanol and Maxsorb III+propane. It can be seen that silica gel+water pair has the highest COP as compared to the other two other pairs even if at low adsorbate loading. At 0.85kg/kg, this pair has the COP of 0.93. The curve trend is very close to that of KOH6-PR+ethanol pair, which might be due to the higher isosteric heat associated to this pair at lower coverage. However, in the case of Maxsorb III+propane, the COP is very low at low uptake and at 0.85 kg/kg, the highest COP is only 0.77.

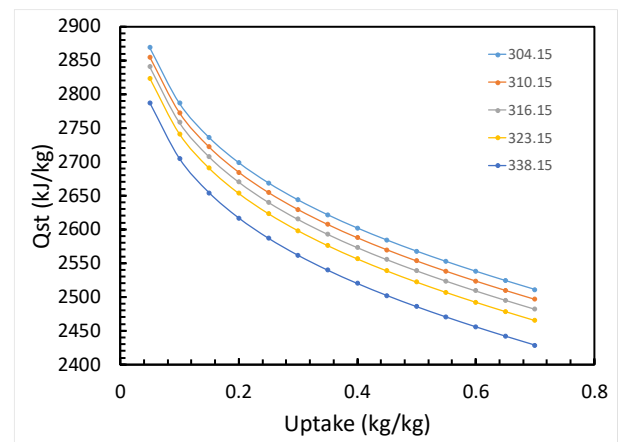


Fig. 2a. Isothermic Heat ( $Q_{st}$ ) for silica gel+water pair against adsorption uptake

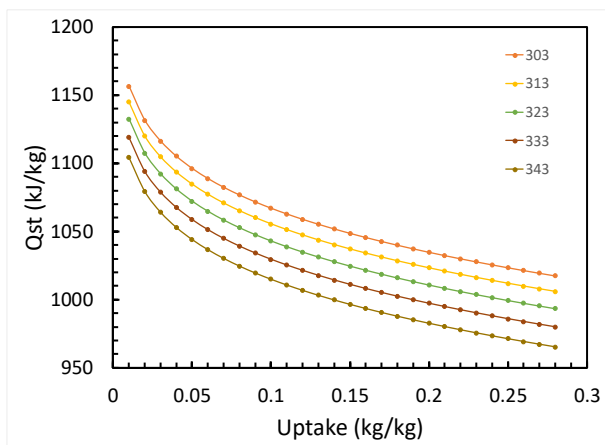


Fig. 2b. Isosteric Heat ( $Q_{st}$ ) for KOH6-PR+ethanol pair against adsorption uptake.

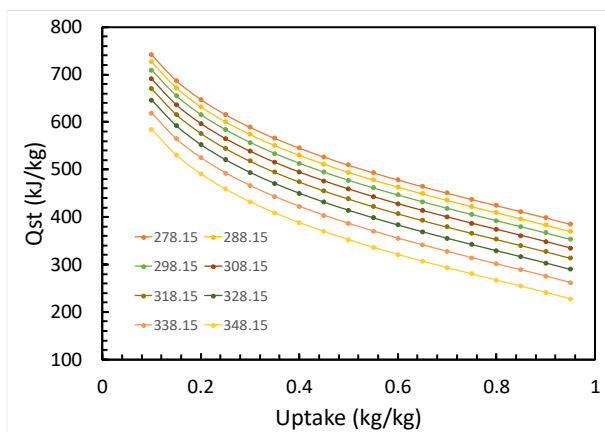


Fig. 2c. Isosteric Heat ( $Q_{st}$ ) for Maxsorb III+propane pair against adsorption uptake

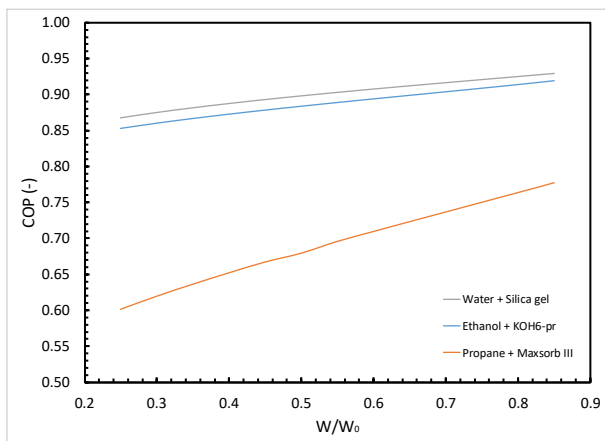


Fig. 3. Coefficient of Performance (COP) versus adsorbate loading ( $W/W_0$ ) of silica gel+water, KOH6-PR+ethanol and Maxsorb III+propane pair.

#### 4. CONCLUSION

The isosteric heat of adsorption is a basic foundation in any adsorptive system in order to assess the performance of the system. Results obtained from this study show that the COP of the system strongly depends on the limiting uptake on a particular adsorbent+adsorbate pair itself. Relatively good agreement has been achieved between the calorimetrically measured experimental work and the form in which  $Q_{st}$  is further derived employing the D-A equation. It is observed that silica gel+water and KOH6-PR+ethanol pairs provide higher theoretical COP values as compared to Maxsorb III+propane pair for the same

coverage. Moreover, these thermodynamic quantities are essential in designing more practical and efficient adsorptive system such as adsorption chiller.

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