Liquid Phase Adsorption of Multi-component Organic Solvent Mixture onto Activated Carbon

Awang Bono, Norina Yadin, NurAbidah Ramlan, Farm Yan Yan, and Chu Chi Ming

***Abstract*—** Liquid phase adsorption is a common technique in separation process. Most of the measurement and analysis of liquid phase adsorption are based on a single component adsorption. However, in the true process most of the adsorption process occurs in multi-component system. Hence, in this work a study of liquid phase adsorption at complete range of concentration for binary and multi-component onto adsorbent was conducted. Organic solvent such as methanol, propanol and acetone were selected as the adsorbate, whereas activated carbon was chosen as the adsorbent. Mixture of binary and three components of solvent were used as the liquid phase for the comparison. The measurement of excess isotherm of using conventional technique for both binary and three components mixture was conducted. The analysis and interpretation of adsorption isotherm were carried out using Gibbs Dividing Plane Model. The results obtained from the analysis of adsorption isotherm for both binary and three components adsorption system found to be significantly different. The effect of binary adsorption and multi-components adsorption can be observed on the shape of excess adsorption isotherm and also on the magnitude of individual adsorption isotherm. Thus, assumption of single component adsorption in multi-components system may lead prediction of unrealistic process.

***Keywords*—** Binary adsorption, Excess Adsorption isotherm, Multi-component adsorption, Gibbs dividing plane

I. INTRODUCTION

SEPARATION or removal of compound of interest from a mixture is one of important process in industries. There are several techniques can be employed for this purposes such as coagulation [1], [2] oxidation [2], [3], filtration, reverse osmosis, ion exchange [3], adsorption [2] and etc. Adsorption is well established compound separation or removal technique, it also known due to the capability of the removal compound from low concentration[4]. Several application adsorption process have been employed for removal of unwanted component from a solution [2], [5], removal the contaminants from wastewaters [4], [6]–[8], separation and purification [1], [2], [8]–[10], removal the unwanted organic and inorganic impurities in drinking waters and waste effluence [11]–[14], removal the odor and taste [11], [12], [15] and removing the color from waste of textile industries [1]. In order to utilize the technology of adsorption process, knowledge in adsorption isotherm and adsorption kinetic are extremely important. Adsorption isotherm can be considered as the most important information in the studies of adsorption process. The information of adsorption isotherm is always required for the basis of analysis, design and prediction of adsorption processes [6]. For example, adsorption isotherm, plays an important role in predictive modeling for analysis and design of adsorption systems [1], [5], and gives useful information, such as determination of surface area, volume of pores, size distribution of adsorbent [16], description of the adsorbate interacts with adsorbent and thus optimizing the adsorption of adsorbent [5], [17] and determination information of relative adsorptivity of a gas or a vapor on a given adsorbent with respect to chosen standards [18].

Investigations and analysis of adsorption are well documented in standard text books and various scientific journals [19]–[21]. Most of measurement of adsorption isotherm, analysis and interpretation are focused on single compound and at low concentration region[22]. The investigation of adsorption isotherm for binary system is also available.[23]. However in the real life, most of the adsorption process occurs in multi-component system. The investigation of multi-component adsorption is rarely can be found and only few investigations reported. The misinterpretation of adsorption isotherm may lead to the prediction of unrealistic process. Therefore, a study on the adsorption equilibrium and interpretation of adsorption isotherm of binary and multi-component was carried out for further understanding the effect of multi-component on adsorption isotherm. Three components mixture was chosen for the representation of multi-component system of adsorption. The study was conducted for the measurement of excess isotherm of adsorption of binary and three component mixture of organic solvent onto activated carbon. The adsorption isotherm was derived from the analysis of excess isotherm using Gibbs

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Dividing Plane model. The analysis results were compared for binary and three components adsorption..

II. MATERIALS AND METHODS

A. Materials

Experimental work was conducted with the utilization of materials such as adsorbent, adsorbates and analytical chemicals. Activated granulate was chosen as the adsorbent and it was purchase from chemical supplier (FLUKA). The mixtures of adsorbates were prepared by mixing of organic solvents of methanol, propanol and acetone. The organic solvents used were analytical grade and were purchased from Fisher Scientific. The composition of the organic solvents mixtures is shown in Table I. The analytical chemical such as helium gas and the analytical column was selected from a common analytical procedure of organics solvent using gas chromatography [9], [24]

TABLE I
BINARY AND MULTI-COMPONENT MIXTURES

Mixture	Component	Preference Adsorbate
Mixture 1	Methanol (Meth) +Propanol (Prop)	Meth
Mixture 2	Methanol (Meth) Acetone (Ace)	Meth
Mixture 3	Methanol (Meth) + Acetone (Ace) +Propanol (Prop)	Meth

B. Excess Adsorption Isotherm

A conventional method of excess adsorption isotherm measurement was employed in this study [9]. The experimental work was conducted by mixing of, 2.0g of activated carbon with 20g of organic solvents mixture in 250ml sealed conical flask. The mixture was left for four hour to reach equilibrium in orbital shaker at 30^{o}C with rotation speed of 100rpm.

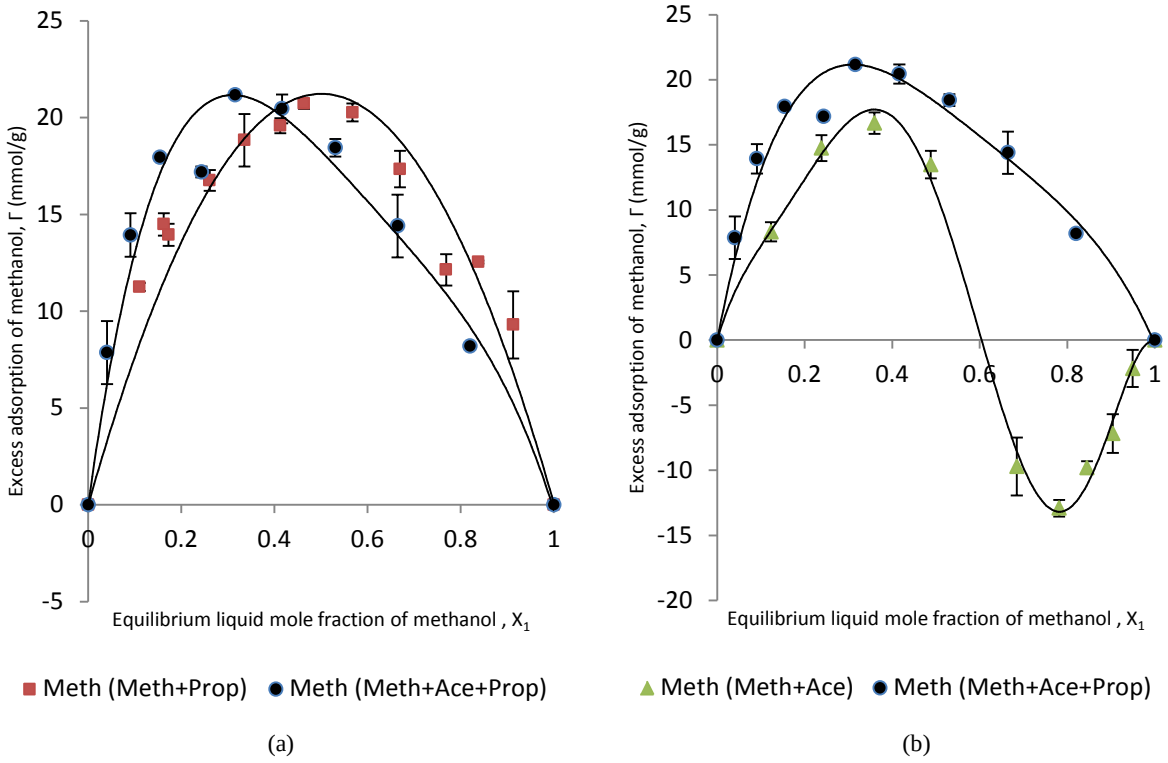
The equilibrated liquid phase was sampled using 0.45µm Whatman syringe filter. Samples were then analyzed using Gas Chromatography Mass Spectrometer (GCMS) to determine the equilibrated liquid composition. The compositions of initial mixture, equilibrated mixture, initial weight and the weight of adsorbent were then used for the determination of the numerical value of excess adsorption isotherm as shown in Equation (1), [19–21] :

$$\Gamma_1 = \frac{W_0(x_{10}-x_1)}{w_s} \quad (1)$$

C. Analytical Procedure of Mixture compositions

The mixture composition was determined using GCMS. Capillary column, 24079 Supelcowax types of column was used with *helium* as carried gas at 35kPa. The injection volume is 1 µL and the flow rate is 1.6mL/min. The oven temperature was programmed as;

- Initial Temperature was kept at 40^{0}C for 2 minute, then ramped 25^{0}C/min to 65^{0}C with holding time for 1 minute and finally ramped 25^{0}C/min to 100^{0}C for holding time for another 1 minute.
- Injection temperature was set at 150^{0}C with 100:1 is split ratio value.



(a) (b)

Fig. 1 Ecxess adsorption isoterm for binary and multi-component organics solvent mixture onto activated carbon at 30^{o}C

Nomenclature

Γ_1	Excess Adsorption of component 1
W_0	Initial total mass of liquid mixture
W_s	Mass of adsorbent
x_{10}	Initial liquid mole fraction of component 1
x_1	Equilibrium liquid mole fraction of component 1
ea_{max}	Maximum adsorbate amount which could be adsorbed on 1 m^2 on the adsorbent surface
$\Gamma(C_e)$	Excess adsorption (in mole/m^2)
(C_e)	Equilibrium concentration
V_a	Surface specific volume of adsorbed phase

III. Adsorption Isotherm Analysis

Gibbs dividing plane model was used for the analysis and interpretation of adsorption isotherm both binary and multi-component mixture. The Gibbs Dividing plane Model as shown in Equations (2) & (3) [25];

A. Maximum adsorbed layer volume:

$$\frac{d\Gamma(C_e)}{d(C_e)} = -V_a \quad (2)$$

B. Total adsorbed amount:

$$a_{tot}(C_e) = \Gamma(C_e) + C_e.V_a \quad (3)$$

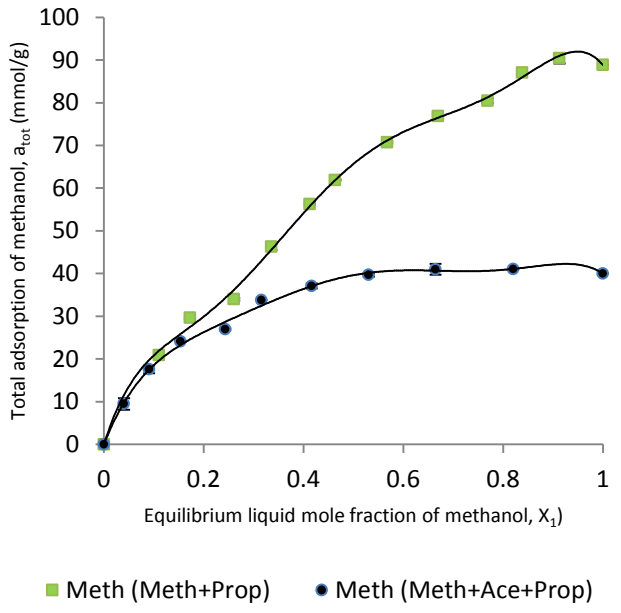
IV. Results and Discussions

The numerical values of excess adsorption isotherms for both binary and multi-component mixture were determined using (1) and shown in Figure 1. Figure 1(a) shows that the excess adsorption of binary mixture (Meth+Prop) and multi-component (Meth+Ace+Prop) onto activated carbon is positive over the whole range of liquid concentration. The shape of excess adsorption isotherm can be confirmed to the type I (U-shaped) adsorption isotherm according to the Schay-Nagy classification [20]. The U-shaped isotherm Tppe I is also indicates that is a preference for only one component of the solution over the entire concentration range [21].

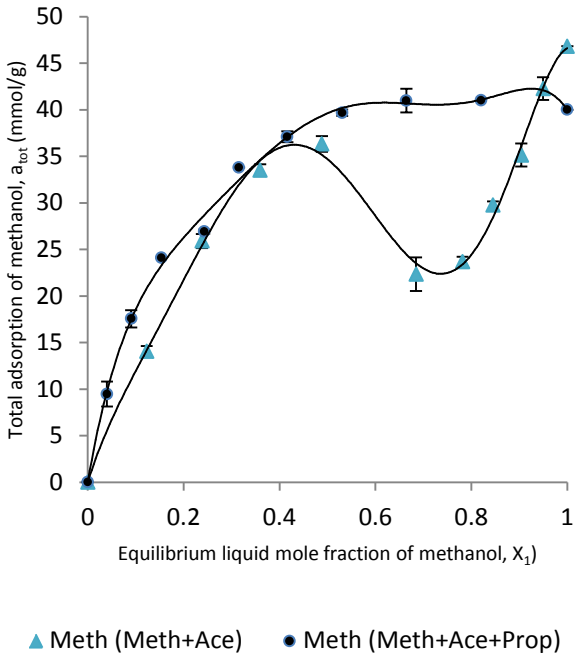
Whereas in Figure 1(b), for binary mixture (Meth+Ace), it shows S shape of excess adsorption isotherm start with positive followed by negative values over the whole range of liquid concentration. This phenomena was due to the azeotropic properties of the liquid mixture. The S shape of excess isotherm of methanol-acetone onto activated carbon can be confirmed to IV (S-shaped) adsorption isotherms classification of Schay-Nagy [20]. The S shape excess adsorption isotherm is also indicates that the surface of activated carbon is preference for both adsorbate in the solution but over different concentration ranges [18].

Fig. 1(b) also shows that the azeotropic properties of methanol and acetone mixture completely disappeared with the addition of third component. Excess adsorption isotherm behavior of three component mixture shows non-azeotropic behavior and significantly different with the excess adsorption isotherm of binary mixture. This trend is similar reported by Swiatkowski et. al, 2004 [24]. Therefore, it revealed that the adsorption isotherm of multi-component mixture is significantly different with binary system and it also changes the adsorptivity of adsorbate.

The result of analysis of adsorption isotherm using the monolayer theory which is Gibbs Dividing Plane Model is shown in Figure 2. This figure is showing the adsorption



(a)



(b)

Fig. 2 Adsorption isotherm of preference adsorbate (methanol) from organics solvent mixture onto activated carbon at 30°C

isotherm of preference adsorbate or Surface specific adsorption isotherm at whole range of liquid concentration for both binary and three components mixtures. The total adsorption of methanol is increasing as the increase of liquid concentration. The adsorptivities of methanol onto activated carbon are significantly different for binary and three components system. The trend of the adsorptions is predominantly monolayer fashion. This is essentially consistent with the same behavior observed previously for the adsorption of the same compound on phenyl modified adsorbents [26].

Fig. 2(a) shows that the adsorption isotherm of methanol in multi-component mixture (Meth+Ace+Prop) is lower than adsorption of binary mixture (Meth+Prop). Whereas, the behavior of methanol adsorption from binary azeotropic mixture showing significant different in the azeotropic region of liquid concentration compared to three component system as shown in Figure 2(b).

V.CONCLUSION

The excess adsorption isotherms of methanol in binary (Methanol+Propanol, Methanol+Acetone) and multi-component system (Methanol+Acetone+Propanol) were measured. The Shape of Excess Adsorption isotherms were confirmed with Schay & Nagy classification. The shape of excess adsorption of methanol in binary and multi-components are significantly different. The adsorption isotherms of preference adsorbate (methanol) were also analyzed and determined using Gibbs Dividing Plane model. The adsorptivites of methanol onto activated carbon over whole range liquid concentration are significantly different for binary and multi-component adsorption. Thus, it shows that there is significant effect on the adsorption isotherm with the existence of other compound in the system.

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