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Effect of ultrasound on liquid phase adsorption of azeotropic and non-azeotropic mixture

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Abstract

Relative adsorption experiments of azeotropic and non-azeotropic mixture were separately conducted at constant temperature with and without the presence of ultrasound. The ultrasound wave was applied at a frequency of 21 kHz with 25% amplitude at atmospheric pressure. The adsorption of azeotropic and non-azeotropic mixture was analysed using monolayer adsorption theory and at lower liquid equilibrium concentration it followed a Langmuir type of equation. The adsorptive capacity of azeotropic and non-azeotropic mixtures on activated carbon was found to decrease but the selectivity was increased. The result also showed that the azeotropic point of relative adsorption was noticeably moved due to the ultrasound effect.

Keywords: Adsorption isotherm; Relative adsorption; Monolayer adsorption; Pseudo-ideal system

1. Introduction

Adsorption process is a well-established technology in chemical engineering industries due to its high separation efficiency and mild operating conditions. Many important processes such as purification, catalysis reaction and bulk separation are currently benefit their applications. However, the low-mass transfer rate and the difficulty of azeotropic adsorption/separation limit its development and application. Ultrasound has been proven to be a very useful tool in intensifying the mass transfer process and breaking the affinity between adsorbate and adsorbent by ultrasonic activation, which made the use of ultrasonics for adsorption/desorption popular [1]. Several researchers have studied the role of the ultrasound on adsorption and desorption processes [2,3]. Hamdaoui et al. [4], investigated the effect of ultrasound on adsorption and desorption of *p*-chlorophenol on granular activated carbon, while Kenneth and Price [5], investigated the effect of pulse ultrasound on the adsorption of Genipoisde onto resin 1300.

Breitbach and Bathen [6] studied the ultrasonic effect on polymeric resins adsorptivity in a fixed bed by varying ultrasonics (frequency, power, etc.) and process parameters (flow rate, temperature, etc.). Most of the previous studies were focused on adsorptive capacity in adsorption/desorption process. However, the selectivity of adsorption and the effect on azeotropic system in the presence of ultrasound have not been studied systematically yet. The selectivity of adsorption is important not only for the separation processes, it is also equally important for the catalysis reactions. The effect of ultrasound on adsorption isotherm of azeotropic and non-azeotropic mixture was studied in this work. Acetone–ethanol mixture was selected as azeotropic mixture and methanol–ethanol mixture for non-azeotropic mixture whereas activated carbon was selected as the adsorbent.

2. Model of binary adsorption system

2.1. Determination of relative adsorption

The relative adsorption for both systems with and without the presence of ultrasound was calculated by using the following equation:

$$\Gamma_1 = \frac{W_0(x_{10} - x_1)}{W_s} \tag{1}$$

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Nomenclature

K	equilibrium constant
n_1^{s}	amount of component 1 adsorbed
n_2^{s}	amount of component 2 adsorbed
N_{s}	saturation adsorption capacity
W_{s}	mass of adsorbent
W_0	initial total mole of liquid mixture
x_1	equilibrium liquid mole fraction of component 1
x_2	equilibrium liquid mole fraction of component 2
x_1^{s}	adsorbed phase mole fraction of component 1
x_2^{s}	adsorbed phase mole fraction of component 2
x_{10}	initial liquid mole fraction of component 1
Greek symbol	
Γ_1	relative adsorption of component 1

By performing a material balance [8–10] the above equation can be simplified as

$$\Gamma_1 = N_{\mathrm{s}}(x_1^{\mathrm{s}} - x_1) \tag{2}$$

For pseudo-ideal system the equilibrium constant can be defined as

$$K = \frac{x_1^{\mathrm{s}} x_2}{x_2^{\mathrm{s}} x_1} \tag{3}$$

Manipulation of the equilibrium equations (Eqs. (2) and (3)), results the following Langmuir type of equation:

$$\frac{x_1 x_2}{\Gamma_1} = \frac{1}{N_{\mathrm{s}}}\left(x_1 + \frac{1}{K-1}\right) \tag{4}$$

The linear plot of Eq. (4) can provide the values of equilibrium constant, K and the adsorption saturation value, N_{s}.

2.2. Determination of individual adsorption

The concentration of adsorbed phase of component 1 can be presented as Eq. (5) by manipulating Eq. (3):

$$x_1^{\mathrm{s}} = \frac{K x_1}{1 + (K-1)x_1} \tag{5}$$

and component 2 can be calculated as $(1 - x_1^{\mathrm{s}})$.

The amount of component 1 adsorbed can be obtained by rewriting Eq. (5) in the form of Eq. (6):

$$n_1^{\mathrm{s}} = N_{\mathrm{s}} \frac{K x_1}{1 + (K-1)x_1} \tag{6}$$

Whereas, component 2 can be written as

$$n_2^{\mathrm{s}} = N_{\mathrm{s}}(1 - x_1^{\mathrm{s}}) \tag{7}$$

The individual adsorption isotherm of binary systems can be calculated using Eq. (6), whereas the selectivity can be presented using Eq. (5).

3. Materials and methods

3.1. Materials

Reagents used were, acetone 99.8%, HPLC grade (Labscan), methanol 99.9% HPLC grade (Mallinckrodt Chemicals), ethanol 99.9% HPLC grade (Mallinckrodt Chemicals) and activated carbon.

3.2. Experimental method

The measurement of relative adsorption was conducted using conventional method [7,8,10], where the known amount of adsorbent W_{s}, was added into initially known concentration x_{10}, and known amount of liquid mixture W_0, in a volumetric flask. The mixture were then left for equilibrium, once equilibrium is achieved the liquid phase was drawn and analysed using gas chromatography to determine the equilibrium liquid concentration, x_1.

For the experiments in the absence of ultrasound, 2.0 g of activated carbon was added into 20 g of mixture. The samples were placed in a temperature controlled water bath shaker at 100 rpm and 30 °C for 4 h for equilibration. Then, 0.2 g of liquid phase was drawn and using 0.45 μm Whatman syringe filter and diluted with 9.8 g solvent before injected to GCMS for analysis. To investigate the effect of ultrasound, the experiment was repeated with the ultrasound as shown in Fig. 1. Ultrasound was applied at the rate of 21 kHz with 25% amplitude.

3.3. Analysis of binary mixture

GCMS was used for the purpose of liquid phase concentration measurement. The GCMS technique was simplified. A HP-5 ms type of column was used with helium as carrier gas at 35 kPa. The volume of sample was 0.05 μL. The flow rate of mobile was used at 1.6 mL/min. The oven temperature was maintained at 65 °C.

4. Results and discussion

The relative adsorption was analysed based on Eq. (4). Fig. 2 shows the relative adsorption of acetone–ethanol on activated

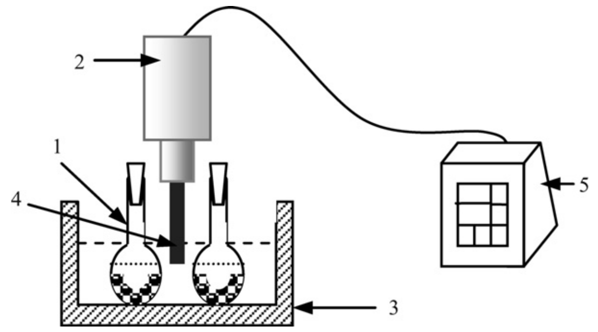

Fig. 1. Experimental set-up for measurement of relative adsorption with ultrasonic: (1) volumetric flask with rubber bung; (2) ultrasonic converter; (3) temperature controlled water bath shaker; (4) ultrasonic probe; and (5) ultrasonic generator.

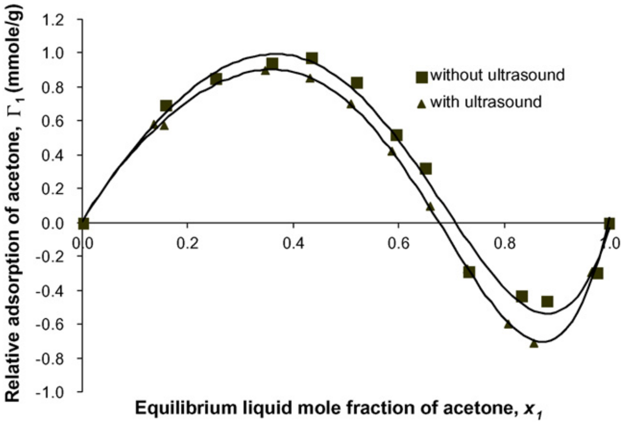

Fig. 2. Comparison of relative adsorptions of acetone–ethanol onto activated carbon at 30 °C.

carbon with and without the presence of ultrasound. In the case of adsorption without the presence of ultrasound the azeotropic point for acetone–ethanol system is approximately 0.72. Whereas in the presence of ultrasound, the azeotropic point is slightly shifted by 0.03 of mole fraction to the left. This phenomena shows that ultrasound has the effect on the azeotropic adsorption. It can be seen that the relative adsorption of acetone in ethanol obtained in the presence of ultrasound is lower than that obtained in the absence of ultrasound as shown in Fig. 2, and the shift is significantly larger than experimental error of mole fraction determination.

In Fig. 3, the relative adsorption of methanol–ethanol onto activated carbon is compared with and without ultrasound. There is no negative adsorption shown in this system. However, the relative adsorption with ultrasound was clearly lowered compared to the case in the absence of ultrasound.

Figs. 4 and 5 represented the adsorption characteristic of binary systems onto activated carbon according to Eq. (4). Figs. 4 and 5 show that at low-liquid concentration both of the binary systems obey Eq. (4). The values of N_s and K obtained from Figs. 4 and 5 with an average regression coefficient of 0.95 are shown in Table 1.

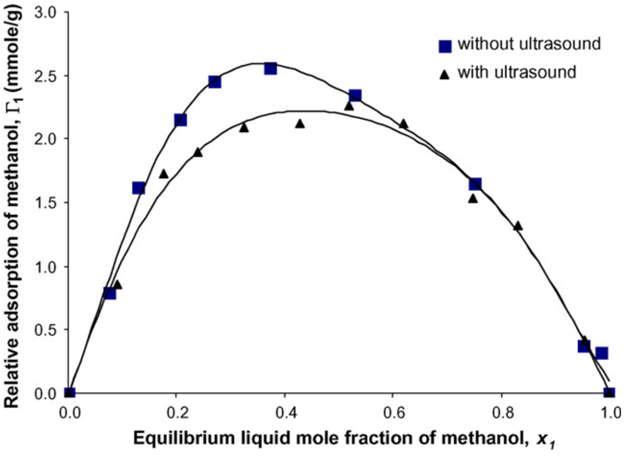

Fig. 3. Comparison of relative adsorptions of methanol–ethanol onto activated carbon at 30 °C.

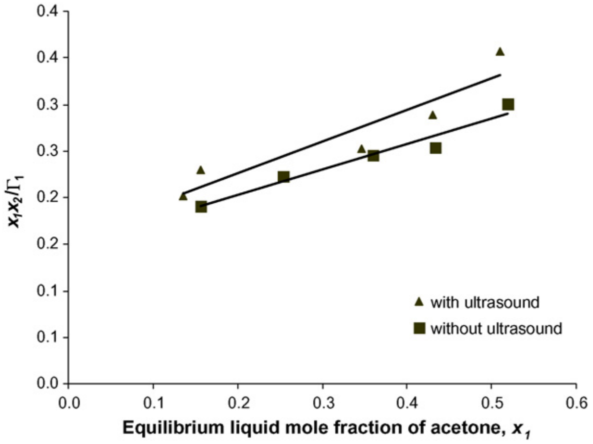

Fig. 4. Apparent conformity of pseudo-ideal monolayer adsorption of acetone–ethanol onto activated carbon.

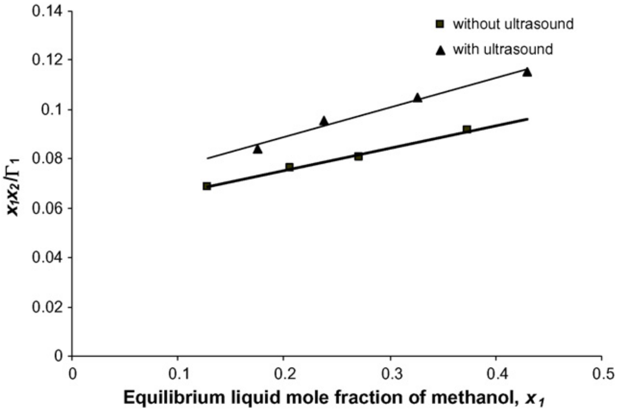

Fig. 5. Apparent conformity of pseudo-ideal monolayer adsorption of methanol–ethanol onto activated carbon.

From Table 1, it is observed that the saturation value of adsorption, N_s was decreased due to ultrasound effect for both azeotropic and non-azeotropic mixtures. In contrast, the equilibrium constant K is increased due to ultrasound effect for both azeotropic and non-azeotropic systems. Recently, similar observation was reported [2].

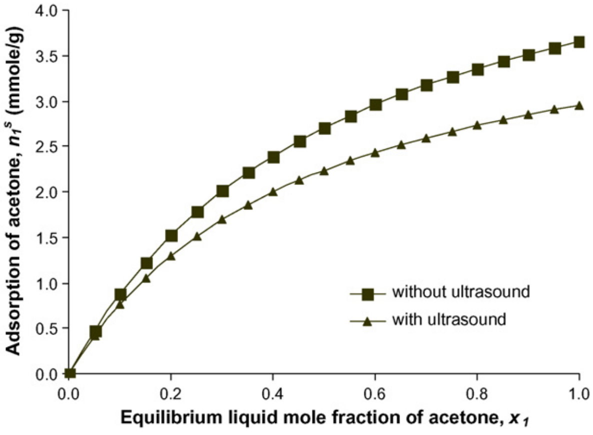

Fig. 6. Individual adsorption isotherm of acetone for (acetone–ethanol) mixture onto activated carbon system at 30 °C.

Table 1
Saturation value of adsorption, N_s and equilibrium constant, K

System	Acetone–ethanol		Methanol–ethanol	
	Without ultrasound	With ultrasound	Without ultrasound	With ultrasound
N_s (mmole/g)	3.65	2.95	11.03	8.25
K	2.85	3.14	2.59	2.88

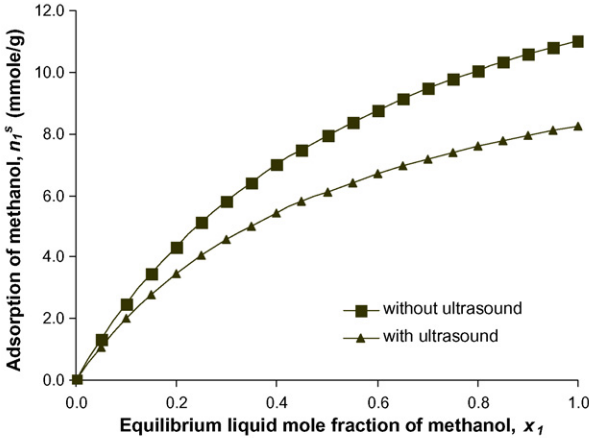

Fig. 7. Individual adsorption isotherms of methanol for (methanol–ethanol) mixture onto activated carbon at 30 °C.

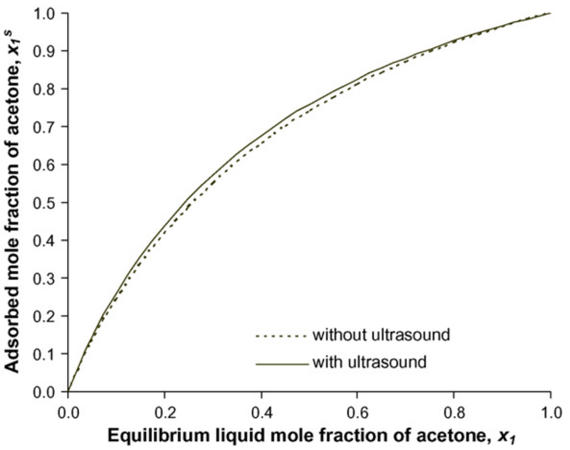

Fig. 8. Selectivity of acetone on activated carbon at 30 °C.

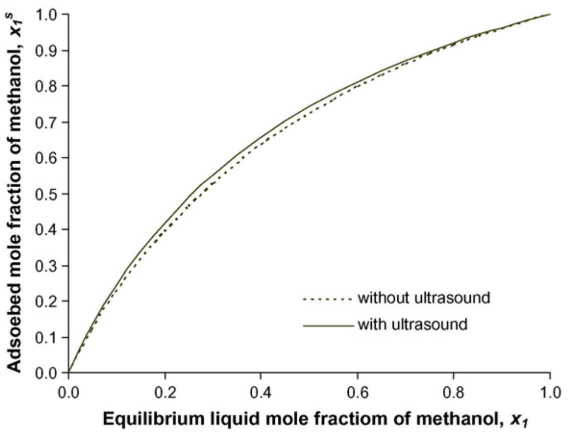

Fig. 9. Selectivity of methanol on activated carbon at 30 °C.

The individual adsorptions of both components in solution were calculated by Eq. (6) and are shown in Figs. 6 and 7. Whereas the selectivity was calculated using Eq. (7) and plotted in Figs. 8 and 9. Fig. 6 clearly shows that the adsorption of acetone is lower in the presence of ultrasound. Similarly, Fig. 7 shows that the adsorption of methanol is lower in the presence of ultrasound.

In the case of selectivity onto activated carbon, there is slight change due to ultrasound. It can be seen in Fig. 8 that the selectivity of acetone onto activated carbon is slightly increased due to ultrasound. Similarly, a trend can be observed in Fig. 9 that the selectivity of methanol onto activated is also slightly increased due to ultrasound.

Several studies have shown that ultrasound decreases the adsorption capacity. This ultrasound phenomenon was explained in terms of generated cavities [1–4]. Ultrasound waves are similar to any other sound waves which consist of cycles of compression and expansion. During the compression cycle, a positive pressure is exerted on the liquid, which pushes the liquid molecules together; and during the expansion cycle, a negative pressure is exerted on the liquid, which separates the liquid molecules away from one another. Sufficient intensity of the sound waves will generate cavities during the expansion period. As the cavity collapses, extreme localize heating with high pressure in less than a microsecond, drives the desorption, thus adsorption decreases at equilibrium.

5. Conclusions

The adsorption of both azeotropic and non-azeotropic systems are lower than in the absence of ultrasound compared to the case in the presence of ultrasound. The effect of ultrasound to cause a shift in the azeotropic point of the adsorbed phase. The adsorption isotherms were well fitted by Langmuir type equation as indicated in Figs. 4 and 5. The results showed that the ultrasound changed the adsorptivity and selectivity of adsorbents. On the other hand, in the presence of ultrasound, the adsorption could enhance higher/greater purity of adsorbed phase. Therefore, further work is required to study the influence of ultrasound on the adsorption characteristics of a wide range of azeotropic and non-azeotropic systems onto various adsorbents.

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