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Effect of Ultrasound on Liquid Phase Adsorption of Azeotropic and Non-azeotropic Mixtures: Generation of Adsorption Isotherms According to Gibbs Dividing Plane Theory

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Abstract: This study conducted adsorption experiments on azeotropic and non-azeotropic mixtures at a constant temperature in the presence and absence of ultrasound. Ultrasound waves were applied at a frequency of 21 kHz and amplitude of 25% at atmospheric pressure. The adsorption of azeotropic and non-azeotropic mixtures was evaluated according to Gibbs dividing plane theory. The results indicated that the adsorptive capacity of azeotropic and non-azeotropic mixtures on activated carbon decreased in the presence of ultrasound.

Key words: Adsorption, Gibbs dividing plane, ultrasonic effect, equilibrium

INTRODUCTION

Adsorption is an important process in the chemical industry. Due to its high adsorption efficiency and mild operating conditions, methods based on adsorption are becoming more popular in catalysis, purification and the bulk separation of materials. To design an efficient adsorption process characterized by high capacity and good selectivity, knowledge of the equilibrium and kinetics of adsorption are required (Ji *et al*., 2006). The adsorption capacity is also paramount because it provides information on the amount of required adsorbent and selectivity is important for catalytic reactions (Joseph *et al*., 2007, 2009; Sircar, 2000).

Limitations to separation processes based on adsorption include low-mass transfer rates and difficulties associated with azeotropic mixtures. Most liquid mixtures of organic components form non-ideal systems, resulting in the formation of azeotropes that may hinder the efficiency of adsorption. Moreover, granular or powdered adsorbents often suffer from relatively low adsorption rates due to their microporous structures and long diffusion paths. The structural requirements of adsorbents place a heavy burden on conventional adsorption processes (Krishnaiah, 2007; Bono *et al*., 2009). Ultrasound has been proven to be a useful tool in enhancing mass transfer and decreasing the affinity of adsorbate to adsorbent. Conventional adsorption often shows a poor capacity and low selectivity for non-azeotropic mixtures and is further complicated by the presence of an azeotrope. These inherent difficulties have led to considerable interest in the development of adsorption processes based on ultrasound. Research has shown that ultrasound decreases the adsorption capacity and enhances the rate of mass transfer (Hamdaoui *et al*., 2008; Li *et al*., 2002; Breitbach and Bathen, 2001; Zhao *et al*., 2008).

Despite the extensive research on adsorption in the presence of ultrasound, experimental and theoretical studies of adsorption equilibria and kinetics present many challenges due to the complexity of adsorption from azeotropic and non-azeotropic mixtures. To better understand the effect of ultrasound on adsorption, a fundamental investigation on the adsorption equilibria of non-azeotropic and azeotropic mixtures must be conducted in the presence and absence of ultrasound. The performance of adsorption is governed by the combined effects of adsorption equilibria and kinetics, which are influenced by the surface and structural characteristics of the solid adsorbent (Rauf *et al*., 2008; Ru *et al*., 2007). The objective of this study was to reveal the effect of ultrasound on different adsorption systems. In a continuation of our recent interest in ultrasound-assisted adsorption of azeotropic and non-azeotropic mixtures (Bono *et al*., 2008), we report herein the generation of adsorption isotherms according to Gibbs

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dividing plane theory. Moreover, the present methodology can be used to predict ultrasonic adsorption data.

MATERIALS AND METHODS

Materials: HPLC grade acetone (99.8%), methanol (99.9%) and ethanol were purchased from Sigma-Aldrich. The adsorbents employed in this study were activated carbon (BET surface area = 800 $m^2 g^{-1}$; average pore size >50 nm) and silicalite zsm-5 (Zeolyst CBV-28014; BET surface area = 345 $m^2 g^{-1}$; average pore size <2 nm). Prior to use, the adsorbents were dried in an oven at 110°C for 24 h and placed in a desiccator.

Analysis: Gas chromatography/mass spectrometry (GC/MS) was used to analyse binary mixtures. Specifically, a simplified GC/MS technique was used to measure the concentration of the adsorbate in the liquid phase. The GC/MS was equipped with an HP-5 MS column and helium at 35 kPa was employed as the carrier gas. The volume of each sample was 0.05 mL and the flow rate of the mobile phase was 1.6 mL min^{-1}. The oven temperature was maintained at 65°C. The operating conditions of the GC/MS are shown in Table 1.

Experimental setup: The experimental setup consisted of an ultrasonic bath, ultrasonic converter, temperature controlled water bath, ultrasonic probe and ultrasonic generator. The experimental setup is shown in Fig. 1. More details on the experimental setup are available in the literature (Sarbatly *et al*., 2009). All the experiments were carried out in triplicate.

Adsorption procedure: The relative adsorption was measured according to a conventional method (Farhadpour and Bono, 1996a, b) in which a known amount of adsorbent, Ws, was added into a volumetric flask with a known concentration of adsorbate, x_{10} and a known volume of a liquid mixture, W_0. The mixture was allowed to achieve equilibrium and the liquid phase was extracted and analysed by gas chromatography to determine the equilibrium concentration of adsorbate, x_1. The amount of adsorbed material was obtained from the following Eq. 1:

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

Where:

Γ_1 = Adsorption of component 1 (mole g^{-1})
W_0 = Initial mass of the liquid mixture (g)

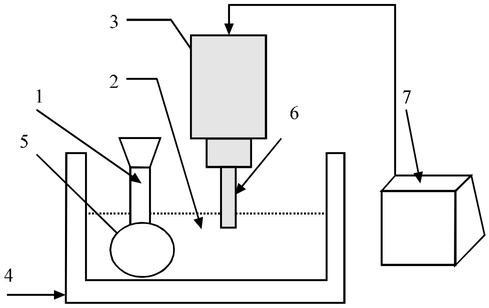

Fig. 1: Schematic diagram of the experimental set-up: 1: Volumetric flask (100 mL) with rubber bung, 2: Water, 30°C, 3: Ultrasonic converter, 4: Isolated water bath, 5 Methanol-ethanol+ZSM-5 6: Ultrasonic probe and 7: Ultrasonic generator

Table 1: GC/MS conditions

Column	HP-5 msec
Carrier gas	He, 35 kPa
Injection volume	0.05 μL
Inlet mode	Splitless
Split ratio	200:1
Column flow rate	1.6 mL min^{-1}
Run time	2.50 min

x_{10} = Initial mass fraction (mole g^{-1})
x_1 = Equilibrium mass fraction (mole g^{-1})
W_s = Mass of adsorbent (g)

Two different sets of experiments were performed, with non-azeotropic and azeotropic mixtures adsorbed onto (1) Activated carbon and (2) Silicalite zsm-5, respectively. The concentration range for methanol-ethanol system and acetone-ethanol systems was 0-0.79 mmole L^{-1} with activated carbon, 0-84.0 with silicalite zsm respectively. In the first (1) set of experiments, 2.0 g of activated carbon was added to 20 g of the liquid mixture in the absence of ultrasound. The samples were placed in a temperature controlled water bath shaker at 100 rpm and 30°C for 4 h to achieve equilibrium. Upon completion, 0.2 g of the liquid phase was extracted with a 0.45 mm Whatman syringe filter and diluted with 9.8 g of solvent. The dilute solution was injected into the GC/MS to determine the concentration of the adsorbate in solution. To investigate the effect of ultrasound, the experiment was repeated in the presence of ultrasound at a rate of 21 kHz and amplitude of 25%.

RESULTS AND DISCUSSION

Generation of isotherms according to Gibbs dividing plane theory: Gibbs dividing plane theory is often invoked to explain the behaviour of liquid phase adsorption (Everett, 1983; Chan *et al.*, 2005; Kazakevich *et al.*, 2001). Gibbs dividing plane theory is a model that is applicable to non-ideal adsorption processes where the adsorbed layer becomes completely filled and the interface between the bulk solution and the adsorbed layer is the hypothetical Gibbs dividing plane.

The amount of adsorbed material can be represented as the sum of the relative adsorption, Γ_{1a} and the product of the equilibrium adsorbate concentration and the volume of the adsorbed layer, $c_1.V_a$. By introducing the specific surface area (per 1 m^2), the relationship can be defined as follows:

$$n^s_{1a} = \Gamma_{1a} + c_1.V_a \quad (2)$$

where, n^s_{1a} is the amount of material adsorbed per square metre of adsorbent surface, Γ_{1a} is the amount of adsorption (mole m^{-2}), c_1 is the equilibrium concentration (mmole L^{-1}) and V_a is the surface specific volume of the adsorbed phase. Therefore, the first derivative of Eq. 2 is:

$$\frac{d\Gamma_{1a}}{dc_1} = -V_a \quad (3)$$

By using the Eq. 2, the amount of adsorbate adsorbed per square metre (n^s_{1a}) of adsorbent was calculated for both azeotropic and non-azeotropic mixtures. Subsequently, n^s_{1a} was multiplied by the surface area of the adsorbent to obtain n^s_{1a} in mole g^{-1}. Individual isotherms were plotted according to the Gibbs dividing plane theory as the mass of adsorbed liquid per unit mass of adsorbent, n^s_{1a}, versus the mass fraction of liquid, x_1. The experimental equilibrium concentration data are shown in Table 2 and 3.

Individual isotherms of non-azeotropic mixtures: The adsorption of non-azeotropic methanol-ethanol mixtures onto activated carbon and silicalite zsm-5 was calculated according to Eq. 1 and 2 and the results are presented in Fig. 2 and 3, respectively. A decrease in adsorption capacity on activated carbon and silicalite ZSM5 was found to be 50, 82.9% respectively in the

Table 2: Equilibrium concentration (methanol-ethanol system)

Activated carbon				Silicalite ZSM5			
Without ultrasound		With ultrasound		Without ultrasound		With ultrasound	
x_1 (g g^{-1})	c_1 (mmole L^{-1})	x_1 (g g^{-1})	c_1 (mmole L^{-1})	x_1 (g g^{-1})	c_1 (mmole L^{-1})	x_1 (g g^{-1})	c_1 (mmole L^{-1})
1.0000	0.7910	1.0000	0.7910	0.0000	0.0000	0.0000	0.0000
0.9859	0.7797	0.9552	0.7551	0.0572	0.0447	0.1230	0.0974
0.9534	0.7536	0.8317	0.6564	0.1556	0.1217	0.2154	0.1724
0.7504	0.5916	0.7471	0.5890	0.2000	0.1566	0.2861	0.2309
0.5299	0.4166	0.5186	0.4887	0.2926	0.2293	0.4180	0.3427
0.3738	0.2933	0.4294	0.4076	0.3093	0.2425	0.4420	0.3634
0.2707	0.2121	0.3257	0.3371	0.3663	0.2874	0.6464	0.5448
0.2063	0.1615	0.2382	0.2554	0.4223	0.3315	0.7433	0.6768
0.1276	0.0998	0.1758	0.1866	0.7485	0.5901	-	-
0.0752	0.0587	0.0905	0.1376	-	-	-	-
0.0000	0.0000	0.0000	0.0000	-	-	-	-

Table 3: Equilibrium concentration (acetone-ethanol system)

Activated carbon				Silicalite ZSM5			
Without ultrasound		With ultrasound		Without ultrasound		With ultrasound	
x_1 (g g^{-1})	c_1 (mmole L^{-1})	x_1 (g g^{-1})	c_1 (mmole L^{-1})	x_1 (g g^{-1})	c_1 (mmole L^{-1})	x_1 (g g^{-1})	c_1 (mmole L^{-1})
1.0000	0.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000
0.9767	0.7910	0.9655	0.7910	0.1261	0.0978	0.0875	0.0680
0.8821	0.7723	0.8558	0.7634	0.2561	0.1974	0.1273	0.0988
0.8329	0.6967	0.8092	0.6757	0.4760	0.3629	0.2180	0.1683
0.7326	0.6573	0.7300	0.6385	0.5942	0.4504	0.3181	0.2444
0.6511	0.5775	0.6597	0.5754	0.7245	0.5456	0.4310	0.3293
0.5947	0.5127	0.5879	0.5195	0.8475	0.6346	0.4927	0.3753
0.5190	0.4079	0.5097	0.4621	-	-	0.5491	0.4171
0.4339	0.3407	0.4311	0.4006	-	-	0.7191	0.5667
0.3598	0.2822	0.3468	0.3385	-	-	-	-
0.2535	0.1986	0.1563	0.2720	-	-	-	-
0.1567	0.1226	0.1356	0.1223	-	-	-	-
0.0000	0.0000	0.0000	0.0000	-	-	-	-

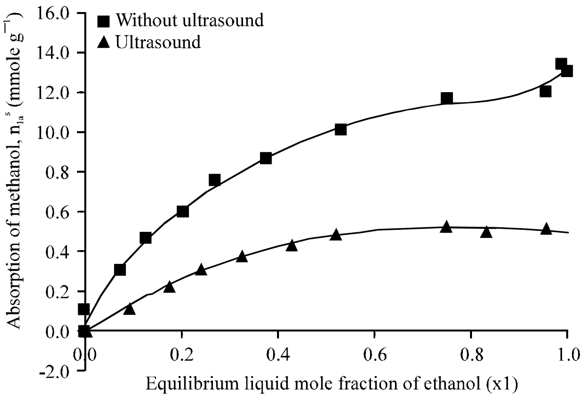

Fig. 2: Adsorption of binary non-azeotropic (methanol-ethanol) mixtures on activated carbon

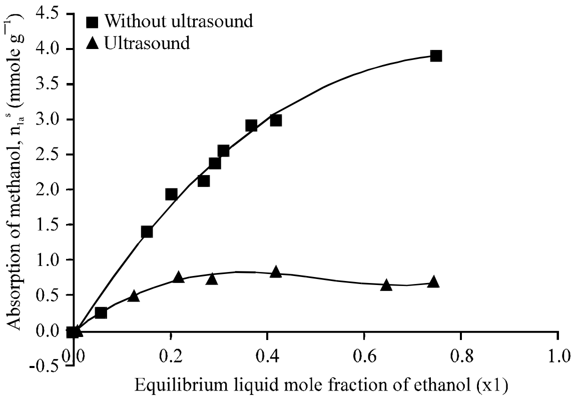

Fig. 3: Adsorption of binary non-azeotropic (methanol-ethanol) mixtures on silicalite ZSM5

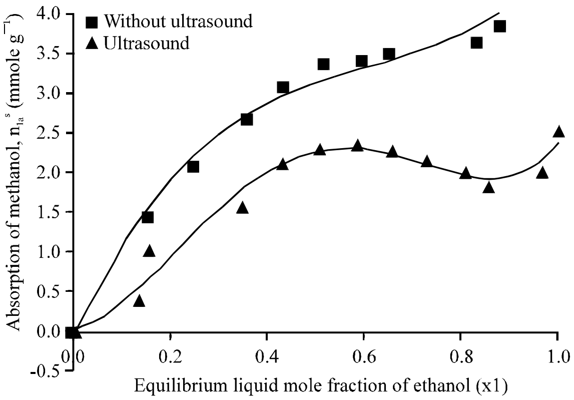

Fig. 4: Adsorption of binary azeotropic (acetone-ethanol) mixtures on activated carbon

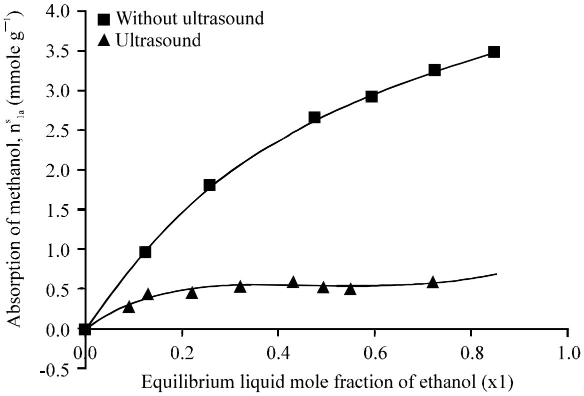

Fig. 5: Adsorption of binary azeotropic (acetone-ethanol) mixtures on silicalite ZSM5

presence of ultrasound. The isotherms observed in the figures are similar to those of previous studies (Chan *et al.*, 2005). Specifically, Fig. 2 and 3 clearly indicate that the adsorption of methanol onto activated carbon is lower in the presence of ultrasound. This could be due to high temperature generated on the surface of adsorbent by the collapse of bubbles by ultrasound (Joseph *et al.*, 2009). In previous studies, the adsorption of methanol was conducted with and without ultrasound and the theory of monolayer adsorption was applied to generate individual isotherms (13), yielding adsorption isotherm trends similar to those in the present study.

Individual isotherms of azeotropic mixtures: Similarly, the adsorption of azeotropic (acetone-ethanol) mixtures onto activated carbon and silicalite zsm-5 was calculated according to Eq. 1 and 2 and the results are shown in Fig. 4 and 5, respectively. A decrease in adsorption capacity on activated carbon and silicalite ZSM5 was found to be 48.0, 82.8%, respectively in the presence of ultrasound. The results clearly indicate that the adsorption of acetone onto activated carbon was lower in the presence of ultrasound. Moreover, the adsorption of methanol was similar to previous results where adsorption was conducted with and without ultrasound (Bono *et al.*, 2008). The adsorption of acetone decreased from 0.5<x1<0.8 but the adsorption increased when x1>0.8. This is due both to the non-thermal and thermal effects of the ultrasonic field and the roles of the latter is much greater than that of the former when x1>1 (Li *et al.*, 2002).

CONCLUSION

This study investigated the adsorption of azeotropic and non-azeotropic systems onto activated carbon and silicalite ZSM-5. The results indicated that ultrasound altered the adsorption of azeotropic and non-azeotropic systems. The adsorption data from azeotropic and non-azeotropic systems were interpreted according to Gibbs dividing plane theory and satisfactory results were achieved.

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