Novel gas chromatographic headspace techniques for measuring Single-component liquid isotherms

Babak Shirani, Mladen Eic *

Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

ABSTRACT

In this study, a novel headspace technique, based on liquid calibration, was developed and compared to the standard headspace or vapor calibration technique. The technique was applied for the measurements of single component liquid adsorption isotherms of xylene isomers, ethylbenzene and toluene on a commercial NaX (13X) zeolite. In comparison to the vapor calibration technique, the liquid calibration technique provided more effective means by faster generating liquid isotherms with more accuracy and less computational complexity. The isotherms were measured at 30, 60 and 90 °C using both headspace techniques, and the results were found reasonably consistent. Among the alkylaromatic compounds studied, the NaX zeolite was more selective to toluene and showed the lowest selectivity to m-xylene. In contrast to larger adsorption capacity of toluene compared to ethylbenzene and p-xylene, the isosteric heats of adsorption indicated that ethylbenzene and p-xylene created stronger bonds to the NaX sites. The effects of solute concentration in the liquid phase were investigated with regard to the adsorption capacity and selectivity. The results indicates that the adsorbent selectivity is generally dependent on the concentration of the solute in the solution.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Xylene isomers, i.e., o-xylene, m-xylene, p-xylene, ethylbenzene and toluene are determined as alkylaromatic components that are widely used in the petrochemical industries as solvents and raw materials. As an example, o-xylene (oX) and m-xylene are respectively used in phthalic and isophthalic acids productions, which are further employed as plasticizers and blends in polymer industries, e.g., PET production [1,2]. Ethylbenzene (EB) is a starting agent in polystyrene production through dehydrogenation reaction to produce styrene [2]. p-xylene (pX) is a major reactant in terephthalic acid production, which is highly demanded in polyester (PET) industries [3–5]. Since the xylene feed stream contains all three isomers and ethylbenzene, it is important to separate these aromatic components and produce high purity isomers to use as raw materials in different industries.

Separation and purification of xylene isomers is a formidable challenge in the industry since their structure and physical properties, i.e., boiling points, are close [6]. Therefore, distillation is only used for o-xylene separation as its boiling point is different from the other two isomers [7,8]. Crystallization is another technology

that is used for xylene isomers separation due to significant differences in the isomers' freezing points [3,9]. Worldwide, about 40% of the p-xylene is produced using this technique since it has the highest freezing point [1,3]. However, besides having a poor efficiency [7], crystallization is not a cost effective method because it requires a large amount of energy to cool down the system to about 220 K [10]. As an alternative, adsorption process, which is cost effective, is widely used to separate xylene isomers [3,10]. Parex and Ebex are the most common industrial adsorption processes for C_8 aromatics separation. In these processes, simulated moving beds are used for p-xylene and ethylbenzene recoveries from the C_8 aromatic mixtures [7,11,12]. About 60% of the p-xylene in the world is produced using adsorption technology [1,9].

The industrial separation of alkylaromatics is carried out in the liquid phase [3,10], thus necessitating information on the equilibria and kinetics of these processes. In contrast to the vapor phase adsorption, where ample literature data are available, a limited number of studies have been conducted to investigate the liquid adsorption, in particular of alkylaromatic compounds. Conventional techniques, such as batch [2,13–15], chromatographic [16] and breakthrough [17] were used to measure adsorption isotherms of some C_8 aromatics isomers in zeolite X and Y. More recently the headspace technique [18–21] was introduced for measurements of liquid adsorption isotherms. In this technique, small quantities of

* Corresponding author.
E-mail address: meic@unb.ca (M. Eic).

the liquid sorbate and a large ratio of solids to liquids are used; therefore, small changes in the liquid concentration can be measured. According to Luna et al. [21], the headspace technique provides accurate equilibrium isotherms at low concentrations.

Considering very limited information available in the open literature, the aim of this study was to investigate the equilibrium and mechanisms of liquid alkylaromatics adsorption, in particular xylene isomers, ethylbenzene and toluene in NaX zeolite. In order to obtain more detailed isotherm information, e.g., from very low concentrations up to the saturation, a novel technique called liquid calibration technique, using GC-headspace apparatus, was introduced in this study. Moreover the results obtained by this technique were compared to the literature results from the vapor calibration technique used by Cavalcante et al. [18–21]. While both techniques were based on sampling the vapor phase in the vial headspace and measuring its composition using the FID detector, different procedures were applied in determining the calibration curves. In the liquid calibration technique, developed in this study, the composition of the liquid phase was determined directly using liquid calibration curve, as explained in the Discussion section of this paper. In addition, the established vapor calibration technique was extended to obtain adsorption isotherms from non-ideal solutions by applying the activity coefficient models required for the VLE calculations. The results obtained by the two techniques were compared and advantages/disadvantages between them discussed in detail.

2. Experimental section

2.1. Reagents

o-xylene (purity > 97%), p-xylene (purity ≥ 99%), m-xylene (purity ≥ 99%), toluene (purity ≥ 99.9%) and decane (purity ≥ 99%) were purchased from Sigma-Aldrich, and ethylbenzene of 99.8% purity was purchased from Acros Organics.

2.2. Adsorbent

NaX (13X) zeolite used in this study was purchased from the Sigma-Aldrich. The adsorbent was in powder form with the particle size of 2 μm shown in Fig. S1 (Section S1 of the supplementary information). Chemical elemental analysis was also performed on the sample, and its result shown in Fig. S2 in the supplementary information; also Si/Al ratio was determined, and its value is revealed in Table 1. The pore size distribution, pore volume and internal surface area were determined from N_2 adsorption isotherm at 77 K using a Belsorp-max (Bell Japan Inc.) instrument. The N_2 isotherm is shown in Fig. S3 (supplementary information, Section S2), and the adsorbent textural properties are summarized in Table 1.

2.3. Experimental setup

A Varian gas chromatograph (450-GC) equipped with an auto sampler was used to determine the vapor phase concentrations in equilibrium with the liquid phase. The auto-sampler device takes the vial from sample tray to the agitator, samples and injects the vapor phase from the vial's headspace into the capillary column. Fig. 1 illustrates a schematics of the experimental setup.

The agitator keeps the temperature of the vial constant, and also, shakes the vial, so that the liquid and vapor phases reach the equilibrium in a short period of time. The washing vials filled with pure solvent were used to clean the syringes after each injection (Fig. 1). In this system, a capillary column (Varian Capillary VF-624 ms) of 30 m length and 0.53 mm inner diameter was used to separate the mixture from the injected sample taken from sample vial. A flame ionization detector (FID), operating at 300 °C, was used to determine the mixture composition. The operating parameters are summarized in Table S1 of the supplementary information.

2.4. Experimental procedures

The NaX particles used in the experiment were regenerated at a temperature of 130 °C under N_2 flow for two days. According to several studies [14,16,22,23], this pre-treatment procedure sufficiently reduces the water content in the zeolite pores (~5%) without affecting adsorption capacity of C_8 aromatics. In addition, it also enhances the selectivity of p-xylene isomer. The adsorbent was then cooled down to room temperature and placed in the vials. Measured quantities of different sorbates and solvent, e.g., n-decane, were added to the vial containing adsorbent particles, upon which the vial was sealed and kept inside the oven for at least 24 h in order to reach equilibrium between the vapor in the headspace part of the vial, liquid and solid phases at a desired experimental temperature.

About half an hour prior to sampling, the vial was placed inside the GC agitator, which was kept at the same temperature as the oven. Using the auto sampler, 100 μl of the vapor phase from the vial's headspace was taken and injected into the capillary column (Fig. 1). Since the vapor phase from the headspace of the vial is sampled and analyzed, this technique is called GC-headspace technique. The syringe was kept at high temperature (Table S1 from the Supplementary part), well above the vials' temperature, in order to prevent the vapor condensation.

Using He as the carrier gas, the aromatic component was separated from the solvent, due to different retention times in the capillary column, and detected with the FID detector (Fig. 1). The results were presented as chromatogram peaks with the area under the peak representing the solute concentration in the solution.

2.4.1. Liquid calibration technique

According to this technique, as developed in this study, the liquid phase composition in contact with the adsorbent was determined utilizing a calibration vial. The vapor phase in the calibration vial containing solvent and sorbate with no adsorbent (Fig. 1), was sampled and analyzed using a standard GC by measuring area under the peak, which was related to the known concentration of the sorbate in the liquid phase. This was repeated for several different concentrations in order to generate the calibration curve.

In order to determine the sorbate concentration in the liquid phase of the sample's vial, containing adsorbent, the sorbate in the vapor phase was sampled and injected into the capillary column. The concentration of sorbate in the liquid phase was then determined by relating the measured peak area to the sorbate liquid concentration using the calibration curve (sorbate's peak area vs. liquid concentration). In the next step, the mass of the sorbate

Table 1
Zeolite 13X textural properties.

Adsorbent	S_{BET} (m²/g)	Total pore volume, v_t from P/P₀ = 0.99 (cm³/g)	Micropore volume from α_s-plot (cm³/g)	Pore diameter (nm)	Si/Al
Zeolite 13X (NaX)	606	0.298	0.285	10	1.23