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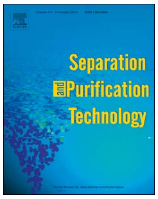

Study on membrane performance in vapor permeation of VOC/N_2 mixtures via modified constant volume/variable pressure method

Wenchao Yang, Haoli Zhou*, Chuanxin Zong, Yuxue Li, Wanqin Jin*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, 5 Xinmofan Road, Nanjing 210009, PR China

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ABSTRACT

Condensation of VOCs in VOC-enriched permeate streams at room temperature in membrane-based VOC/N_2 separation make accurate measurement of membrane separation performance difficult. Membrane performance is important for obtaining fundamental data for industrial applications. Therefore, in this work, a modified constant volume/variable pressure method was developed to avoid the effects of VOC condensation in the permeate and to accurately determine membrane performance for the separation of VOC/N_2 mixtures. Development of the method is discussed and validated by measuring the separation performances of p-xylene/N_2 mixtures using a PDMS/ceramic composite membrane, which showed good reliability. Effects of feed concentration, feed flow rate, and temperature on separation performance were investigated by this method for the separation of representative VOC pollutants such as acetone, p-xylene, ethanol, and ethyl acetate. The permeabilities of VOC and N_2 and their interaction was easily obtained, which open the possibility of the investigation of the interactions between VOC and N_2 during vapor permeation.

1. Introduction

Volatile organic compounds (VOCs) are widely used in chemical processes, which make emission unavoidable because of the difficulty of operation under air-tight conditions. Escaping VOCs affect the health of human beings and also cause economic losses [1]. It is therefore necessary to develop an appropriate technology to recover and reuse escaped VOCs to reduce air pollution. Membrane-based VOC recovery technology is a possible solution [2].

Many membrane materials have been synthesized for application in membrane-based VOC recovery technology to improve the membrane separation performance, which affects the process design and cost of industrial application [3,4]. However, besides the importance of the development of a new membrane, accurate determination of permeate concentration is also important especially in the separation of condensable VOCs/N_2 mixtures, because the easy condensation of VOCs in VOC-enriched permeate streams complicate accurate measurement, which would affect the measurement of membrane performance and finally the technology design in the process of industrialization. Many indirect methods have been developed to analyze the compositions of permeate streams. Feng et al. [5,6] used an indirect method to measure permeate composition. The permeation rates of air and organic vapor were separately determined using a bubble flow meter in the absence of organic vapor and the collected liquefied organics weighted over a period of time. It was assumed that the permeation rate of air was not affected by the presence of organic vapors. The ratio of the permeation rates of air and organic vapors and the permeate composition was obtained by solving a set of equations. Liu et al. [7,8] directly measured the compositions of permeate streams under vacuum using a GC equipped with a six-port sampling valve and a large sampling loop. Li et al. [9] employed the principle of mass balance to calculate permeate compositions. When the flow rate and concentration in the feed and permeate were measured using a flow meter and GC, respectively, the permeate flow rate and concentration were obtained by solving two mass balance equations. Different measuring methods have been developed for the detection of permeate concentration, indicating the difficulty of measurement of condensable VOCs streams. Furthermore, the accuracy of these methods has not been studied. It is necessary to develop a reasonable measurement method that can be widely adopted without any assumptions to accurately determine the permeate compositions. So that the intrinsic separation performance of the membrane and the coupling phenomenon of VOC and N_2 occurred in the separation could be obtained for designing technologies for industrial application and for the investigation of the separation mechanism of condensable VOC/N_2 mixtures in gas/vapor separation.

A constant volume/variable pressure method has already been widely used to determine the diffusion coefficient and permeability of steady-state pure gas, pure vapor, and gas/gas mixtures, as it is

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* Corresponding authors.
E-mail addresses: zhouhl@njtech.edu.cn (H. Zhou), wqjin@njtech.edu.cn (W. Jin).

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independent of gas type [10–16]. Deveci et al. [13] were the first to use this method to investigate the diffusion coefficient of oxygen gas passing through thick-walled polypropylene copolymer pipes. The order of magnitude of the oxygen gas diffusion coefficient through the polypropylene pipe was $10^{-11}\,m^2\,s^{-1}$, which was consistent with the value measured by other processing methods [17]. Roman et al. [14] studied the effects of water vapor on gas permeability using a modified constant volume/variable pressure method. Using this method, gas permeability of a dense polymeric membrane can be easily determined in the presence of water vapor, with a total uncertainty of 5–10%. The permeability obtained at low humidity was consistent with that obtained under dry conditions by the classic time-lag method, indicating the reliability of this method. Sohn et al. [15] used this method to determine the permeability of pure gas and pure organic vapor through a hexamethyldisiloxane membrane, which shows that this method can measure the permeability of gas/vapor mixtures and it is independent of gas type. While in membrane-based VOCs recovery systems, both organic vapors and gases exist in the permeate at low vacuum pressures. Therefore, a modified constant volume/variable pressure method was used to determine the permeability of gas/vapor mixtures in the permeate, which could avoid the condensability of VOCs in the permeate due to high vacuum. And to the best of our knowledge, the measurement of permeability of permeate gas/vapor mixtures using this method has not yet been reported.

In this study, a constant volume/variable pressure method coupled with a gravimetric method was successfully established to analyze the separation performances of a series of condensable VOC/N_2 mixtures permeated through thin film PDMS/ceramic composite membranes. Ethanol, p-xylene, acetone, ethyl acetate, mesitylene and four paraffin compounds were chosen as the representative VOCs. The effects of feed VOC concentration, flow rate and operating temperature on the separation performance of the PDMS/ceramic composite membrane were investigated. The coupling effect was analyzed by comparing the permeabilities of individual nitrogen component in the mixtures with pure N_2 permeability.

2. Experimental

2.1 Materials.

PDMS/ceramic composite membrane was supplied by Nanjing Jiusi High-tech Co. Ltd China. They were 140 mm in length with the external diameter of 12 mm and the inner diameter of 8 mm. The PDMS layer with the thickness of 4 μm faced the VOC/N_2 feed during the separation experiments. N_2 (99.999% pure) was purchased from Nanjing Special Gas Factory Co., Ltd, China. Ethanol, p-xylene, mesitylene, acetone, ethyl acetate, cyclohexane, n-octane, n-heptane and n-hexane used as vapor solvents (99%+) were purchased from Sinopharm Chemical Reagent Co., Ltd, China and were used without further purification.

2.2. Experimental apparatus

2.2.1. Vapor permeation

The experimental apparatus is shown in Fig. 1. A pure N_2 stream was introduced to the vapor generator in an isothermal bath containing liquid VOC. N_2 was bubbled through the liquid VOC in the generator. A N_2 diffuser under the liquid VOC was used to make fine gas bubbles in the generator. The generated VOC/N_2 stream was blended with a second pure N_2 stream to produce mixture streams of desired composition and flow rate. The compositions and flow rates of the mixtures were controlled by adjusting the flow rates of the first and second N_2 streams using a mass-flow controller (MFC; D08-2F, SEVENSTAR). After the mixtures were generated, they were admitted to the membrane cell at atmospheric pressure. The effective area of tube composite membrane used was 47 cm^2. The membrane cell was placed in a water bath to keep its temperature constant. All connection nuts were sealed with double O-rings to assure tightness of tubing installation and leaks were tested with a soapy liquid before beginning the experiment. The compositions of the feed and residue streams were measured using a gas chromatograph (GC-2014, SHIMADZU) equipped with two detectors: an FID detector for VOC and a TCD detector for N_2. The permeate pressure was maintained below 1000 Pa by a vacuum pump (D8C, LEYBOLD) and was constant for a certain period of time to attain the steady state. The permeated VOC was collected in a cold trap at a given time and weighed using a digital analytical balance. The alternate use of two cold traps between the permeation cell and vacuum pump allowed the permeated VOCs to be continuously sampled and recovered at all times.

The performance of a membrane is usually expressed in terms of permeate flux *J,* which is calculated as follows:

$$J = \frac{W}{At} \tag{1}$$

Where W is the weight of the permeate component, A is the effective area of the membrane, and t is the time interval for permeation.

The permeate flux is dependent on the operating conditions. Normalizing the permeate flux in reference to the driving force for permeation helps understand the permeation-specific intrinsic membrane properties. The intrinsic membrane property is permeability P_i:

$$P_i = \frac{J_i L}{(X_{feed} P_{feed}) - (X_{perm} P_{perm})} \tag{2}$$

where L is the film thickness (cm), X_{feed} and X_{perm} are the mole fractions of compound i in the feed and permeate streams, J_i is the flux of compound i, and P_{feed} and P_{perm} are the feed and permeate pressures (cmHg), respectively. X_{perm} is the only unknown value in Eq. (2).

The selectivity (α) was calculated and expressed by the expression:

$$\alpha = \frac{P_{VOC}}{P_{N_2}} \tag{3}$$

where $Pvoc$ and P_{N2} are the permeabilities of VOC and N_2, respectively.

2.2.2. Principle of the constant volume/variable pressure method

The diagrammatic sketch for VOC/N_2 permeation measurement setup by the constant volume/variable pressure method is shown in Fig. 2a. The setup was composed of a membrane cell, a defined permeate test vessel, and a vacuum pump. Two pressure transducers – one installed in the feed line and the other in the permeate line – were used to record the pressure change. The pressure transducer in the permeate (CDG025D and VGC501, INFICON) was equipped with a capacitive sensor element made of aluminum oxide ceramic and electronics, which converted the capacitance to a DC voltage output signal. The output signal was linear to the measured pressure and independent of gas type.

Before measurement, the test vessel was evacuated with a vacuum pump. A VOC/N_2 mixture with a certain constant concentration and constant feed pressure was continuously introduced into the membrane cell. When the system reached the steady state, valve B was closed. The mixture that permeated through the membrane caused the pressure to increase slowly with time in the permeate test vessel. The time-dependent permeate pressure increase is presented qualitatively in Fig. 2b, which shows that the permeate pressure increased slowly until it became equal to the feed pressure, suggesting that the permeation rate of the VOC/N_2 mixture decreased with time. The permeate pressure changed a little at the beginning of the measurement, but linearly increased with time, indicating an almost constant permeation rate. The permeabilities of the mixtures or single compound can be determined from the slope of the linear portion of the permeate pressure increase with time using Eq. (4) [18]: