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Sorption of trifluoromethane in zeolites and ionic liquid

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ABSTRACT

Sorption isotherms for trifluoromethane (R-23) on three zeolites, Na-Y, K,H-Y, and Rb,Na-Y and ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf_2N] have been measured at ca. 298 and 323 K, using a gravimetric microbalance. The adsorption on the zeolites reaches about 3 $mol \cdot kg^{-1}$ at 0.025 MPa and 298 K while in the ionic liquid the absorption reaches 3 $mol \cdot kg^{-1}$ at about 2.5 MPa (100 times higher pressure). Three different adsorption models (Langmuir, multi-site Langmuir, and BET equations) have been used to analyze the zeolite sorption data, with a particular interest in the heat of adsorption ($-\Delta H$). The heat of adsorption for zeolites Na-Y, K,H-Y, and Rb,Na-Y were about 35 ± 3 $kJ \cdot mol^{-1}$, 29 ± 3 $kJ \cdot mol^{-1}$, and 34 ± 5 $kJ \cdot mol^{-1}$, respectively. These values are within the range of typical physical adsorption. According to the IUPAC classification, the zeolites exhibit Type II adsorption and according to the Scott and van Konynenburg classification the ionic liquid is predicted to be Type V phase behavior. The adsorption process on the zeolites took more time than the absorption process in the ionic liquid to reach the thermodynamic equilibrium and both processes were reversible.

1. Introduction

Trifluoromethane (CHF_3, R-23) is a by-product from the manufacture of chlorodifluoromethane ($CHClF_2$, R-22) which is used as a refrigerant in air-conditioning applications and as a feedstock for the production of tetrafluoroethylene ($F_2C=CF_2$, TFE). R-23 is essentially an unwanted by-product due to its high global-warming potential. In our original work [1], we studied three zeolites (5A (Ca,Na-A), 13X (Na-X) and Na,K-LSX) and an ionic liquid ([omim][TFES]) to capture R-23 from a vent stream. In the present work, we study the adsorption behavior of R-23 with three additional zeolites (Na-Y, K,H-Y, and Rb,Na-Y) and an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]), at about 298 and 323 K from 0.001 to 2 MPa. To the best of our knowledge, such work has never been reported in the literature. Zeolites are micro-porous, aluminosilicate materials commonly used as commercial adsorbents [2] and ionic liquids are a relatively new class of salts which are liquids at room temperature. We believe that zeolites and ionic liquids have the potential of providing precise and specific separation of gases such as the removal of fluorocarbons from air and nitrogen waste streams.

Recently, Olah and coworkers at the University of Southern California have figured out how to use R-23 as a fluorinating agent [3]. They found that using the base potassium hexamethyldisilazide in tetrahydrofuran solvent will activate the C–H bond in R-23 (CHF_3). Several reactions to other intermediates have been proposed such as adding elemental sulfur to R-23 to produce trifluoromethanesulfonic acid (CF_3SO_3H). This work may make it possible to utilize the R-23 by-product captured from the R-22 process.

The present adsorption data of R-23 on zeolites have been analyzed using three adsorption models with a particular interest in calculating the heat of adsorption: (1) Langmuir [4], (2) multi-site Langmuir [5,6], and (3) BET [7] equations. In addition to the above adsorption studies, we have investigated absorption (VLE:(vapor + liquid) equilibria) of R-23 in ionic liquid [emim][Tf_2N]. VLE data have been correlated well with our generic RK (Redlich-Kwong) equation of state (EOS) model [8]. Results are compared with the present adsorption data on zeolites in the R-23 molality *versus* pressure plot and comparisons with our previous work are also discussed.

2. Experimental

2.1. Materials

Trifluoromethane (R-23, CHF_3, purity >99.995%, molecular weight 70.014 $g \cdot mol^{-1}$, CAS No. 75-46-7) was purchased from GTS-Welco (Allentown, PA). Zeolite Na-Y, ($Na_{56}[(AlO_2)_{54}(SiO_2)_{138}]$, formula weight 12,782.2 $g \cdot mol^{-1}$), zeolite K,H-Y ($K_{43}H_{10}Na_1[(AlO_2)_{54}(SiO_2)_{138}]$, formula weight 13,201.9 $g \cdot mol^{-1}$), and zeolite Rb,Na-Y ($Rb_{39}Na_{17}[(AlO_2)_{57}(SiO_2)_{135}]$, formula weight 15,154.6 $g \cdot mol^{-1}$) were prepared as described below. The 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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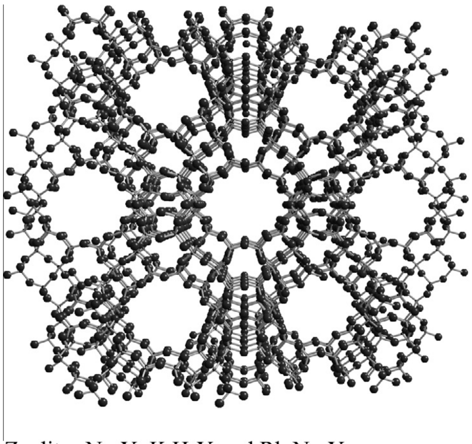
([emim][Tf$_2$N], $C_8H_{11}F_6N_3O_4S_2$, assay ⩾99.5%, molecular weight 391.31 g · mol^{-1}) was purchased from Covalent Associates (Corvallis, OR). The aluminosilicate frameworks of the zeolites and the chemical structure of the ionic liquid are shown in figure 1.

Zeolite Na-Y was prepared by adding a mixture of 135 g $NaAlO_2$, 100 g NaOH, and 700 g H_2O to 1000 g Ludox® LS-30. The resulting gelatinous material was shaken and allowed to stand at room temperature for 72 h. Next, the solution was placed in an oven at 363 K for 48 to 72 h. After the heated time was completed, the solution was filtered, washed and dried overnight. X-ray powder diffraction of the resultant powder verified the product material to be zeolite Na-Y.

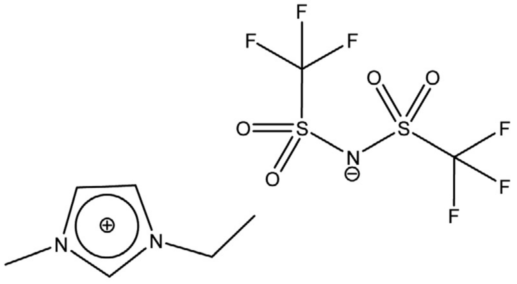
Zeolite K,H-Y was prepared by contacting 100 g of zeolite NH_4-Y (LZ-Y62 (Union Carbide (Linde): lot 968184061086-8-8)) with a 10 wt% aqueous solution of KNO_3 (10 mL/g of zeolite) at 363 K for 1 h and filtering after the exchange. K,H-Y was ion exchanged a total of three times and after the final exchange the solids were filtered, washed, and dried.

Zeolite Rb,Na-Y was prepared by contacting 100 g of zeolite Na-Y (LZ-Y52 (Union Carbide (Linde): lot 111885)) with a 10 wt% aqueous solution of Rb-acetate (10 mL/g of zeolite) at 363 K for 24 h and filtering and drying after the exchange. Rb,Na-Y was ion exchanged a total of three times and after the final exchange the solids were filtered, washed, and dried.

All the zeolites were activated by heating a sample in a vertical tube furnace at 623 K for 12 h under vacuum. The zeolite elemental analyses reported above were obtained using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The BET surface area for the zeolites Na-Y, K,H-Y, and Rb,Na-Y was measured and found to be 624, 598, and 525 m^2 · g^{-1}, respectively. The total pore volume for the zeolites Na-Y, K,H-Y, and Rb,Na-Y was also measured and found to be 0.358, 0.318, and 0.279 cm^3 · g^{-1}, respectively (see table S7 in Supplementary data).



Zeolites Na-Y, K,H-Y and Rb,Na-Y



1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[emim][Tf$_2$N]

FIGURE 1. Aluminosilicate framework structure of the zeolites Na-Y, K,H-Y, and Rb,Na-Y and the chemical structure of the ionic liquid ([emim][Tf$_2$N]).

The mass fraction of water in the [emim][Tf$_2$N] was measured by Karl-Fischer titration (AquaStar® C3000, solutions AquaStar® Coulomat C and A). The [emim][Tf$_2$N] was dried and degassed by filling a borosilicate glass tube with about 10 g of ionic liquid and pulling a coarse vacuum with a diaphragm pump (Pfeiffer, model MVP055-3, Nashua, NH) for about 3 h. Next, the [emim][Tf$_2$N] was completely evacuated using a turbopump (Pfeiffer, model TSH-071) to a pressure of about 5×10^{-6} kPa while simultaneously heating and stirring the ionic liquid at a temperature of about 333 K for 5 days. The final mass fraction of water was measured by Karl-Fischer titration and the dried sample contained less than 0.0150 ± 0.001 mass% H_2O (150 ± 10 ppm H_2O). The [emim][Tf$_2$N] sample was further purified under vacuum at a temperature of 348 K using the microbalance to remove trace amounts of water as described in the next section. A detailed description of the (vapor + liquid)-equilibria (VLE) and (vapor + liquid + liquid)-equilibria (VLLE) equipment and procedures are available in our previous reports [8–12]. Therefore, only the basic experimental techniques and measurement uncertainties are given here.

2.2. (Vapor + liquid) equilibria and adsorption measurements using a gravimetric microbalance

A gravimetric microbalance is a common method used to measure the solubility of gases in sorbents. The method was originally developed to accurately measure the gas adsorption on solids (e.g., zeolites); however, it can also be used to measure the gas absorption in ionic liquids due to their low vapor pressure. We have extensively used a Hiden gravimetric microbalance (IGA003) [13] to measure the solubility and diffusivity of many different gases (CO_2, SO_2, hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs)) in ionic liquids over a range of temperatures (283 to 348 K) and pressures (0 to 2 MPa) [14–26]. The advantages of using a microbalance include the minimal sample size (<100 mg) required, the ability to automate the measurement process to take several *PTx* data, and the flexibility to measure both absorption and desorption isotherms. When done properly, the gravimetric analysis provides a direct and accurate method for assessing both gas solubility and diffusivity [9]. Two critical factors that must be considered include properly correcting for the buoyancy effects of the system and allowing sufficient time to reach equilibrium (i.e., no mixing is possible) [10]. In particular, the sorption of gases on zeolites and liquids is a diffusion-controlled gas sorption process which can take several hours or days to reach equilibrium at a given *T* and *P*. The critical details for properly correcting for a number of balance forces are provided in the following references [9,10,26].

The adsorption and desorption measurements were performed in static mode in this study. The sample temperature was measured with a resistance temperature device (RTD) with an accuracy of ±0.1 K. The RTD was calibrated using a standard platinum resistance thermometer (SPRT model 5699, Hart Scientific, American Fork, UT, range 73 to 933 K) and readout (Blackstack model 1560 with SPRT module 2560). The Blackstack instrument and SPRT are a certified secondary temperature standard with a NIST traceable accuracy to ±0.005 K. Two isotherms of about 298 and 323 K were measured beginning with 298 K. Two pressure sensors were used for the measurements. Pressures from (10^{-4} to 10^{-2}) MPa were measured using a capacitance manometer (MKS, model Baratron® 626A) with an accuracy of ±0.015 kPa. Pressures from (10^{-2} to 2.0) MPa were measured using a piezo-resistive strain gage (Druck, model PDCR4010) with an accuracy of ±0.8 kPa. The Druck low-pressure transducer was calibrated against a Paroscientific