

Gas Drying Using Supported Ionic Liquids

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Supported ionic liquids are promising pseudo-adsorbents for gas drying processes. They are produced by impregnation of hygroscopic ionic liquids with low vapor pressures on silica surfaces. A screening of potential alternatives to [EMIM][MeSO₃] revealed that [EMIM][TFA] is sufficiently hygroscopic but not thermally stable enough for technical use. [EMIM]Cl shows, compared to [EMIM][MeSO₃], a higher affinity for water absorption, but is less stable as well as corrosive. [EMIM][OTf] shows high thermal stability, but has an insufficient low activity coefficient of water, so that [EMIM][MeSO₃] remains most promising. Water sorption isotherms and measurements of breakthrough curves in a bench scale fixed-bed adsorber confirmed, that depending on the operating conditions, the capacity for water can be increased in a supported system of [EMIM][MeSO₃] impregnated on Silica 90, compared to adsorption at the pure silica surface. Exceptionally for medium to low partial pressures of water, supported systems appear to be favourable for adsorption processes. The shapes of the breakthrough curves of pure silica and the supported system are similar, what indicates similar or only slightly increased mass transport resistances due to the impregnation.

1. Introduction

Gas drying and purification processes are of interest in several industrial branches, especially for natural gas dehydration and exhaust gas treatment (Kohl & Nielsen, 1997). If the content of water vapor, respectively the dew point, is too high, the formation of water can lead to corrosion and blocking of pipelines by clathrate hydrates. Although absorption processes are prevalent for gas drying, in demand of a low residual water content and medium to little feed gas flow rates, adsorption plants exhibit high economical potential (Mersmann et al., 2000) and low requirement for space. The most commonly used adsorbents for water are silica gel, activated alumina and molecular sieves, mostly applied in fixed-bed adsorber plants.

A novel approach, presented in this article, is to immobilize hygroscopic ionic liquids on silica gel and use this combination as a pseudo-adsorbent for water.

Ionic liquids (ILs) represent new and promising solvents, e.g. for homogeneous (two-phase) catalysis (Wasserscheid, 2000), separation processes like extractions (Boesmann et al., 2001) as well as engineering (Zhao, 2006). The advantage of ionic liquids compared to common organic solvents is their often extremely low vapor pressure, which make them attractive for separation processes, since losses by evaporation and therefore impurities in product streams are avoided. Immobilization of ionic liquids on support materials has already been carried out in the context of SILP (Supported Ionic Liquid Phase) (Mehnert et al., 2002) and SCILL (Supported Catalyst with Ionic Liquid Layer) (Kernchen et al., 2007) for catalytic purposes.

Several ILs, like those investigated in this study, show very hygroscopic behaviour. Even small amounts of water in hygroscopic ionic liquids (ppm range), strongly affect their material properties such as density, kinematic viscosity, activity coefficient, catalytic activity and electrical conductivity (Martins et al., 2013). At elevated temperatures, changes in the chemical structure of ILs can occur by thermal decomposition (Heym et al., 2015a) or by hydrolysis (Wasserscheid & Welton, 2008).

However, the property of hygroscopic ILs to bind water strongly can be proved advantageous for gas drying by absorption, wherefore up to today glycols, such as triethylene glycol (TEG), are commonly used. Continuous gas dehydration experiments in a bench scale absorption plant using pure ionic liquids showed promising results (Krannich et al., 2016a).

Ionic liquids exhibit still better handling as adsorbents in supported state than in liquid phase due to often high viscosity, high melting points and, as may be the case, corrosiveness. In the present work a screening of the relevant physical and chemical properties for a gas drying process by supported ionic liquids is conducted. The ionic liquid [EMIM][MeSO₃] was already characterized for its suitability as drying agent for technical gas dehydration processes in previous works (Krannich et al., 2016b). As potentially even more suitable ionic liquids [EMIM]Cl, [EMIM][TFA] and [EMIM][OTF] were chosen for further investigations.

2. Experimental Methods

2.1 Screening of Ionic Liquids for gas drying

In addition to [EMIM][MeSO₃], which was already characterized as drying agent, three more hygroscopic ILs were investigated: 1-Ethyl-3-methylimidazolium chloride [EMIM]Cl, 1-Ethyl-3-methylimidazolium trifluoroacetate [EMIM][TFA] and 1-Ethyl-3-methylimidazolium trifluoromethane sulfonate [EMIM][OTF]. Suppliers, purities and melting points of these ionic liquids are given in Table 1.

Table 1: Ionic Liquids investigated in this work

Chemical Name	Source	Mass fraction purity wt %	Melting point (pure IL) K
[EMIM][MeSO ₃]	Sigma-Aldrich	95	306
[EMIM][TFA]	Sigma-Aldrich	98	223
[EMIM][OTF]	Sigma-Aldrich	98	260
[EMIM]Cl	Iolitec	98	360

The properties of interest for later use in supported state are the activity coefficient of water in the respective ionic liquid and their thermal stability.

The activity coefficient ($\gamma_{H_2O,IL}$) of water in the IL was determined by different measurement methods, but was always calculated by Raoult's law:

$$\gamma_{H_2O,IL} = \frac{p_{H_2O}}{x_{H_2O} \cdot p_{H_2O}^0(T)} \quad (1)$$

where x_{H_2O} is the molar fraction of water in the ionic liquid, $p_{H_2O}^0(T)$ the saturation vapor pressure of (pure) water at the prevailing temperature T and p_{H_2O} the partial pressure of water above the IL.

The activity coefficients of water in [EMIM][TFA] and [EMIM][OTF] were measured employing a quartz crystal microbalance (QCM). The experimental setup consists of a gas dosing system for nitrogen (99.999 % purity), a flow-through water saturator, and a temperature-controlled measuring chamber (± 1 K) with the QCM (RQCM from Inficon; frequency error < 1 Hz) and a humidity sensor (HYT 221 from IST). A quartz crystal with unpolished chromium/gold electrode for operating temperatures to 363 K from Inficon was applied. Detailed information to the setup, methodology and the applicability of the QCM-method for ILs were already published (Schmidt & Heym, 2017). After determining the resonance frequency of the clean crystal in flowing dry nitrogen, the electrode of the QCM was coated with a thin film of the ionic liquid by wetness impregnation using dichloromethane as solvent (DCM; purity p.a., Sigma Aldrich). After that, the IL-coated quartz crystal was exposed to dry nitrogen until the resonance frequency became constant, which meant the elimination of residual water, DCM and impurities in the sample. Subsequently the coated crystal was exposed to various partial-to-saturation pressure ratios p/p_0 of water, what is equal to the relative humidity in the measuring chamber. By means of the shifts of the resonance frequencies of dry clean, dry coated and wet IL films, the molar water content x_{H_2O} and therefore the activity coefficients can be calculated.

The activity coefficient of water in [EMIM]Cl could not be measured with the QCM-method, because it was found that this IL leads to damage of the chromium/gold electrode. For this reason the activity coefficient of water in [EMIM]Cl was measured with a magnetic suspension balance (MSB) from Rubotherm. As a first step, the IL was dried in the MSB under vacuum by 368 K for at least 24 h. After this conditioning phase, when a constant mass (signal) was reached, a defined partial pressure of water was adjusted in the temperature-controlled measuring chamber (± 0.5 K) by making a connection to a temperature-controlled water saturator. The partial pressure of water, the temperature of the measuring chamber and the mass increase by water absorption in [EMIM]Cl (mass signal) were recorded.

The kinetics of thermal decomposition of [EMIM]Cl and [EMIM][TFA] were determined at atmospheric pressure in a horizontal thermobalance Exstar 6300 from Hitachi High-Tech. Each IL was dried and purified

during a conditioning phase before the thermogravimetical analysis (TGA) at 383 K for 3 h. The experiments were conducted with N₂ (99.999 % purity) or He (99.996 % purity) at heating rates of 0.1 K/min, 2 K/min and 10 K/min. Two different carrier gases were necessary to exclude evaporation of the ionic liquids (Heym et al., 2015a). Quartz glass crucibles were used, and the gas flow rate was always 5.6 l/h (STP). The detailed analysis of TGA experiments with ILs is described in previous works (Heym et al., 2015a). The kinetic parameters of thermal decomposition were determined from the curves of weight loss versus temperature (constant heating rate), thereby assuming a first order reaction. With these parameters the maximum operation temperature $T_{max,decomposition}$ for the respective fluid can be determined for a maximum reasonable degree of conversion X_{IL} due to thermal decomposition in a given timespan t :

$$T_{max,decomp,X/t} = \frac{E_{A,IL}}{R} ((\ln(t) + \ln(k_0)) - \ln(-\ln(1 - X_{IL})))^{-1} \quad (2)$$

Where k_0 is the pre-exponential factor of reaction rate constant by Arrhenius equation in 1/s, $E_{A,IL}$ is the activation energy of thermal decomposition, R is the gas constant 8.314 J/(mol K), T is the temperature in K.

2.2 Preparation of Supported Ionic Liquids and Water Sorption Isotherms

For the investigations in supported state, [EMIM][MeSO₃] was coated on Silica 90 (Sigma-Aldrich; $d_{pore} = 9$ nm $V_{pore,0} = 0.88$ cm³/g), pre-dried at 453 K for 16 h. Before impregnation, the IL was dried in a rotary evaporator in high vacuum for at least 16 h to remove water and other impurities. The water content of the IL was measured with a Karl-Fischer-Titrator 831 KF (Metrohm) and was always below 0.5 wt %. The preparation of the supported ionic liquids was performed following to the wetness impregnation method of Fehrmann (Fehrmann et al., 2014). To characterize the generated supported IL systems, the pore filling degree α is introduced:

$$\alpha = \frac{V_{IL}}{V_{pore,0}} \quad (3)$$

where V_{IL} is the volume of ionic liquid in the supported system per gram of dry silica and $V_{pore,0}$ the initial specific pore volume.

The water sorption isotherms of the samples were measured with the static volumetric sorption analyzer Autosorb IQ (Quantachrome) with vapor dosing option. Since the water content can rise during storage, each sample was conditioned under vacuum (< 0.1 mbar) at 373 K for 16 h, except of pure silica gel, which was dried at 453 K for 16 h in an oven to avoid changes of its surface chemistry.

2.3 Fixed-Bed Adsorber Measurements

A flow chart of the experimental setup for fixed bed measurements of pure Silica 90 and [EMIM][MeSO₃] supported on Silica 90 is shown in Figure 1.

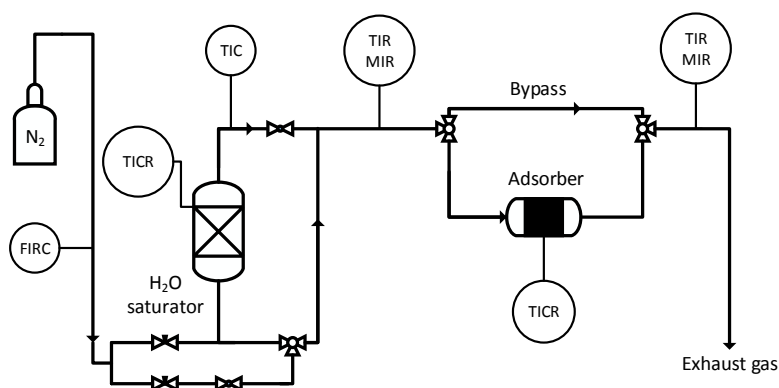


Figure 1: Flow chart of the experimental setup for the adsorption measurement of water in supported systems

The setup consists of a gas dosing system for nitrogen (99.999 % purity), a water saturator and a temperature controlled tubular fixed-bed adsorber (± 0.5 K). The moisture content was measured at the inlet and the outlet of the adsorber with humidity sensors (HYT 221 from IST). As first step, each particle bed was purged several hours by dry nitrogen for conditioning before starting the measurement. The measurements were conducted at atmospheric pressure with particles of 0.3 – 0.5 mm diameter, bed lengths of 10.8 cm and a 9 l/h volume flow (STP).

3. Results and Discussion

3.1 Screening of Ionic Liquids

The activity coefficients of water in [EMIM]Cl, [EMIM][TFA], [EMIM][OTF] and the approximated curve for [EMIM][MeSO₃] (Krannich et al., 2016a) are shown in Figure 2.

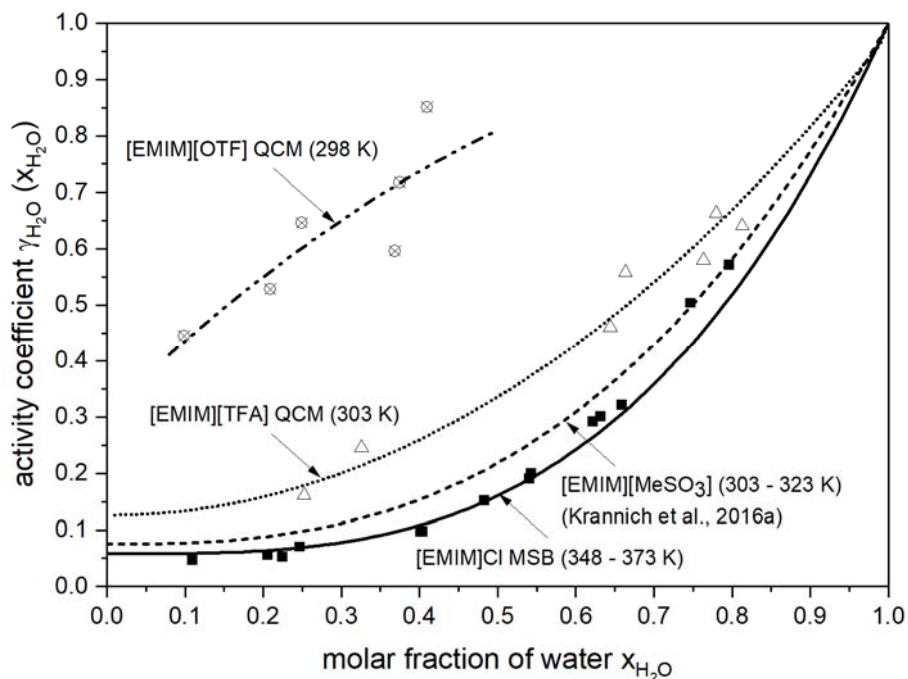


Figure 2: Activity coefficients of water in the investigated ionic liquids

For high water contents, a value of $\gamma_{H_2O,IL}$ of one is approached as expected by Raoult's law. At low contents the value approaches an almost constant value, the infinite dilution activity coefficient. [EMIM]Cl shows a very high affinity to water and therefore low values of the activity coefficient versus molar fraction. Due to its high melting point, it had to be heated to 348 K under vacuum for conditioning and for measurements in liquid phase. To obtain measurements with low molar fractions of water in [EMIM]Cl, the measuring chamber had to be heated up to 373 K to achieve low partial-to-saturation pressure ratios. However, as it can be seen the temperature influence on $\gamma_{H_2O,IL}$ is small and almost negligible.

The QCM measurements show a wider dispersion of measurement points due to the high temperature sensitivity of the method. [EMIM][TFA] shows a little less hygroscopic behavior compared to [EMIM][MeSO₃], what could be sufficient enough for absorption as well as favorable for the desorption of water in a regeneration step. [EMIM][OTF] was verified to be less hygroscopic, therefore insufficient for gas drying and with its small amount of absorbed water even elaborate to measure in the range of validity of QCM.

The thermal stabilities of the ILs are shown in Table 2 as maximum operation temperatures for industrial use of 1 % per year.

Table 2: Maximum operation temperature for use in gas drying

	[EMIM]Cl	[EMIM][TFA]	[EMIM][OTF]	[EMIM][MeSO ₃]
$T_{max,decomp,1\%/a}$ in K	349	300	482	434
			(Heym et al., 2015b)	(Krannich et al., 2016b)

The in this article determined maximum operation temperature of 349 K for [EMIM]Cl is in good agreement with the calculated 347 K with kinetic data by decomposition under argon in literature (Efimova et al., 2015). [EMIM][TFA] shows an especially low maximum operation temperature due to an anion-centred decarboxylation mechanism, enabled by the stable CF₃⁻ anion that would be formed (Clough et al., 2013). The maximum operation temperatures of [EMIM][OTF] and [EMIM][MeSO₃] were already published and show sufficient thermal stability for an application as drying agent. Summarizing, [EMIM][MeSO₃] is still the most promising IL for gas drying because of the low thermal stability of [EMIM][TFA] and the modest thermal

stability of [EMIM]Cl, which was additionally found to be very corrosive and damages the silica support. Hence, only [EMIM][MeSO₃] is examined in the following.

3.2 Water sorption isotherms

The sorption isotherms of pure Silica 90, [EMIM][MeSO₃] on Silica 90 with a pore filling degree of $\alpha = 0.3$ and pure [EMIM][MeSO₃], referred to the same mass of dry support material for comparison, are shown in Figure 3.

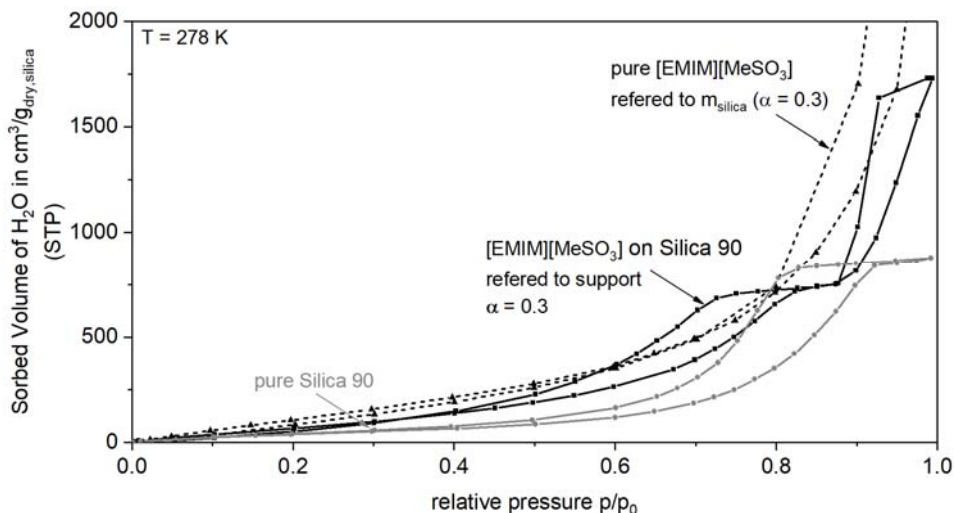


Figure 3: Water sorption isotherms for pure Silica 90, pure [EMIM][MeSO₃] and [EMIM][MeSO₃] on Silica 90

From low relative pressures up to 0.5, which is the region of technical importance for adsorption, the water capacity of the supported system is higher than for pure silica. The supported system almost agrees to the pure IL, what reveals a noticeable but slight effect of the support and it shows the occurrence of hysteresis. Hysteresis is shifted to lower relative pressures than for pure silica. Above the region of technical importance (high relative pressures) the mixture of water and IL seems to flow out of the pores because they are completely filled.

3.3 Breakthrough curves

In Figure 4 the breakthrough curves of pure Silica 90 and [EMIM][MeSO₃] on Silica 90 $\alpha = 0.3$ at a common temperature for adsorption are shown.

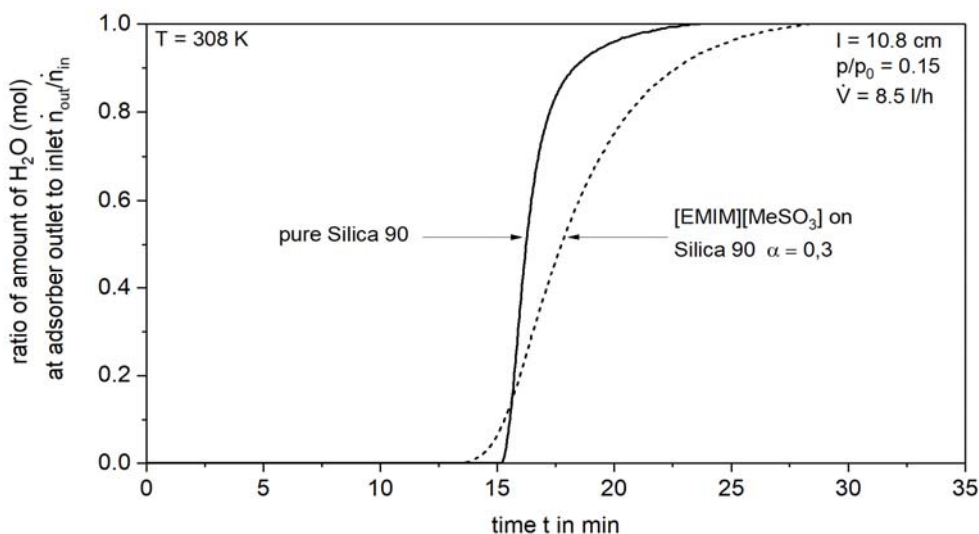


Figure 4: Breakthrough curves of water of pure Silica 90 and [EMIM][MeSO₃] supported on Silica 90

Confirmative to the isotherms in Figure 3 the capacity of sorbed water, what corresponds to the area between the breakthrough curve and the y axis, agrees for the pure Silica 90 and the supported system for an operating point of $p/p_0 = 0.15$. For higher relative pressures, the supported system becomes favorable concerning water capacity. The shape of the curve of the supported system is steep and similar to the form of the pure Silica 90. This small zone of mass transfer (Mass Transfer Zone, MTZ) indicates similar or rather just slightly increased mass transfer resistances, due to the insertion of ionic liquid in the pore system, for the sorption of water in [EMIM][MeSO₃] coated on Silica 90 under the applied measurement conditions

4. Conclusion

Supported ionic liquids seem very promising for gas drying processes in fixed-bed adsorbers. After the investigation of a wide range of ionic liquids in the present and previous works of Heym (Heym et al., 2015b) and Krannich (Krannich et al., 2016b), [EMIM][MeSO₃] is in total of its physical-chemical properties still the most promising drying agent. Water sorption isotherms as well as breakthrough curves of [EMIM][MeSO₃] impregnated on Silica 90 show, depending on the operating conditions, equal alternatively an enhanced capacity of water compared to the pure silica gel. Especially for low and medium amounts of water in feed gas, i.e. medium to low relative pressures and dew points, the supported system is favourable. This proves to be advantageous for adsorption processes, which are commonly used for feed gases with already low water contents and in demand of very low residual water content in the product gas.

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