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A New Application of Acetate-Based Ionic Liquids: Potential Usage as Drying Materials

Acetate-based ionic liquids (AcILs) are green and designable solvents applied in many fields. However, AcILs are found to be highly hygroscopic. On the one hand, the high hygroscopicity of AcILs influences their properties and structures. On the other hand, this hygroscopic property renders AcILs, and especially [EMIM][Ac], potentially useful as drying materials, a new application of AcILs proposed in this paper. These two traits could be interconnected, interdependent, and interconvertible, which implies that a shortcoming of AcILs, i.e., their hygroscopicity, leading to changes in their physical properties, could be turned into a useful feature, e.g., the potential usage as drying material, if it is dealt with properly.

Keywords: Drying materials, Ionic liquids, Property change

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1 Introduction

Ionic liquids (ILs) are organic salts composed of an organic cation and an organic or inorganic anion, and their melting points are normally at less than 100 °C [1]. ILs are 'designable' due to their high tunability by altering the cation, anion, or both [2]. They are also 'green' because of negligible vapor pressure compared to the volatile organic compounds (VOC) under normal operating conditions [3, 4]. Thus ILs have attracted much attention in many fields, such as electrochemistry [5], synthesis and reaction [6–8], and extraction and separation processes [9–15]. Moreover, ILs have potential applications in the chemical industry, as lubricants [16], operating fluids [17], and plasticizers [18].

Acetate-based ILs (AcILs), in particular, have been paid more attention because they have a large CO₂ absorption capacity [19–21] and a favorable dissolution of biomass, e.g., cellulose, chitosan [22, 23]. In terms of CO₂ capture, AcILs could absorb CO₂ at as much as 0.2:1 mol mol⁻¹ CO₂/IL, which is higher than the value for the other, conventional ILs under the same conditions [19–21]. AcILs are also among the best candidates to dissolve cellulose, owing to their desirable properties, e.g., low viscosity, low corrosiveness, low melting point, and favorable biodegradability [24, 25]. Actually, 1-methyl-3-ethyl-imidazolium acetate ([EMIM][Ac]) has already been applied in the industry, by BASF, to dispose of cellulose [25].

ILs (either hydrophobic or hydrophilic ILs) could take up some water from the moisture in air [26–31]. Moreover, mixing with water would affect their chemical structure [32–34] and physical properties [35–37], and thus the potential application of ILs (including AcILs) [38–41]. Water can be deemed as the antisolvent or cosolvent to affect the solubility of solutes in ILs. Contacting with water can hardly be avoided for ILs because water is ubiquitous as moisture in air (humidity). Particularly, among all the ILs, AcILs are more hygroscopic than other kinds of ILs [28], suggesting that water might have a more significant effect on the structure and properties of AcILs. Thus, investigations on the hygroscopicity of AcILs are highly necessary.

However, reports on the hygroscopicity of AcILs are limited. To the best of our knowledge, only the water sorption by 1-methyl-3-butyl-imidazolium acetate ([BMIM][Ac]) and *N*-butylpyridinium acetate ([BPy][Ac]) was reported to be 15.36 and 11.85 % H₂O/IL, respectively, within 3 h at 23 °C and 52 % relative humidity (RH) [28]. We need more data on the hygroscopicity of AcILs to gain a better understanding on the effect of humidity on AcILs.

Herein, the hygroscopicity of five AcILs (Tab. 1) varying in alkyl chain length ([EMIM][Ac], [BMIM][Ac], [HMIM][Ac], [OMIM][Ac]) and C2-methylation ([BMMIM][Ac]) was investigated by directly exposing them to the moisture in air within 40 h. Then, investigations on the changes in the density and viscosity of AcILs in the presence of water were carried out.

More importantly, our experimental results showed that AcILs were very hygroscopic (especially [EMIM][Ac]). Our previous study had also shown a relatively higher hygroscopicity of AcILs compared to other kinds of ILs [28]. Therefore, the possibility of using AcILs (especially [EMIM][Ac]) as drying materials was proposed. Another cue for using AcILs as

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Table 1. Abbreviations, structures, notations, and names of the five AcILs investigated.

No.	Abbreviation	Structure and notation	Name
1	[EMIM][Ac]		1-methyl-3-ethyl-imidazolium acetate
2	[BMIM][Ac]		1-methyl-3-butyl-imidazolium acetate
3	[HMIM][Ac]		1-methyl-3-hexyl-imidazolium acetate
4	[OMIM][Ac]		1-methyl-3-octyl-imidazolium acetate
5	[BMMIM][Ac]		1,2-dimethyl-3-butyl-imidazolium acetate

drying materials came from the reports of Jess [42]. He concluded that the low water vapor pressures of mixtures of water with ILs, i.e., 1-methyl-3-ethyl-imidazolium ethyl sulfate ([EMIM][EtSO₄]) and 1-butyl-3-ethyl-imidazolium ethyl sulfate ([BEIM][EtSO₄]), indicated the possibility of gas dehydration by ILs [42]; however, the highly hygroscopic AcILs have not been investigated. So, in this paper, the potential of the highly hygroscopic AcILs to be used as drying materials was investigated.

2 Experimental

2.1 Materials

The five AcILs (purity >98.5 %) shown in Tab. 1 were purchased from Lanzhou Greenchem ILs, LICP, CAS (Lanzhou, China). They were dried in a vacuum oven at 50 °C for 96 h before use. Then, the water contents (less than 316 ppm, measured by Karl Fisher titration; ZDJ-400S multifunctional titrator, Beijing Xianqu Weifeng Company, Beijing, China), halogen ions (undetectable, measured by AgNO₃ precipitation), and other impurities (undetectable, measured by nuclear magnetic resonance (NMR); Bruker AM 400 MHz spectrometer) were determined. Four drying materials (silica gel, P₂O₅, anhydrous MgSO₄, and anhydrous CaCl₂) with a purity of >99 % were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. They were also dried at 50 °C for 96 h before use. Decomposition of the AcILs during the drying process was not detectable, by comparison of the NMR and infrared (IR) spectra before and after drying.

2.2 Water Sorption

The water sorption processes of the AcILs were conducted by simultaneously exposing the five AcILs to the moisture in air in a closed weighing room for 40 h, with a hygrothermograph sensor (± 0.2 °C and ± 2 % RH accuracy; Testo 608-H2, Germany) nearby. This closed weighing room helped to maintain a relatively stable temperature $T^{(1)}$ ($\mu_T = 25.3$ °C, $\delta_T = 0.18$ °C) and RH ($\mu_{RH} = 35.3$ %, $\delta_{RH} = 0.17$ %) (Fig. 1) within 40 h, where μ and δ indicate the mean value and standard deviation, respectively. The masses of the five AcILs before and after ab-

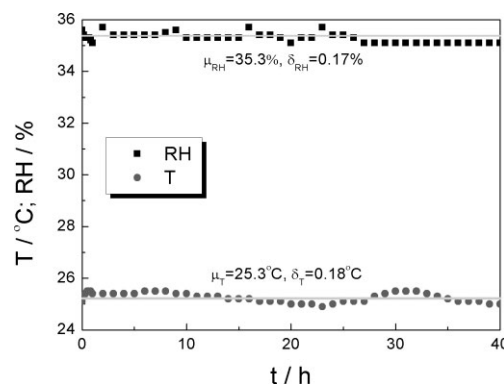


Figure 1. Recorded temperature (T) and relative humidity (RH) of air as a function of time within 40 h when measuring the hygroscopicity of AcILs. The mean values (μ) and standard deviations (δ) of T and RH are 25.3 °C, 0.18 °C and 35.3 %, 0.17 %, respectively. The mean values of T and RH are displayed as solid lines.

1) List of symbols at the end of the paper.

sorbing water from the moisture in air were measured by five specimens of the same kind of analytic balance (± 0.1 mg; Adventure AR224CN, Ohaus). In a typical experiment, the AcILs (cal. 0.4 g) were placed as evenly distributed as possible and without stirring on the bottom of the same kind of glass bottle (5 mL volume and 1.54 cm^2 surface) with already zero setting on the analytic balance. The temperature, RH, and mass were recorded for about 40 h, i.e. every 10 min in the first 1 h and every 30 min for the remaining 39 h. The mass ratio of water to IL ($W_{\text{H}_2\text{O}}$) was used to indicate the water concentration in the water/AcIL mixture.

Note that the absorption of gas, e.g., CO_2 and N_2 , and other impurities, e.g., dust particles, from the air by AcILs could be ignored. This is because of the negligible amount of gas and impurities when compared with the absorbed water from air; the IR spectra showed a slight shift, but no new spectra appeared, indicating that no detectable impurities were absorbed from the moisture in air. Therefore, the increase in mass of the AcILs exposed to the moisture in air could all be attributed to absorbed water.

2.3 Density and Viscosity Measurement

The densities of the AcIL/ H_2O mixtures were measured by a DMA 5000 densitometer (Anton Paar Co., Austria). It was calibrated with dry air and ultrapure water. Additionally, the temperature was controlled by a thermostat with an accuracy of ± 0.001 K. Meanwhile, the dynamic viscosities of the corresponding AcIL/ H_2O mixtures were determined by an AMVn viscosity meter (Anton Paar Co., Austria). The temperature was controlled by a built-in precise Peltier thermostat, with an uncertainty of ± 0.01 K. During the experiments, the density and viscosity data were measured three times and the respective average value was recorded.

2.4 Attenuated Total Reflection-IR Spectra

The attenuated total reflection (ATR)-IR spectra of the AcILs before and after water absorption from the moisture in air were recorded in a Prestige-21 Fourier transform IR (FTIR) spectrometer (Shimadzu, Japan) with a deuterated triglycine sulfate (DTGS) detector around room temperature ($\sim 25^\circ\text{C}$). For each sample, 40 scans were made. The resolution was 4 cm^{-1} ; the wave number was in the range of $4600\text{--}400\text{ cm}^{-1}$. The ATR cell (ATR-8200H) was made of a ZnSe crystal with the incident angles of 45° . On top of the crystal, the AcILs were placed to cover the 584-mm^2 surface. The sample was scanned every 10 min within 1 h, and then every 2 h in the remaining 8 h at room temperature.

3 Results and Discussion

AcILs are very hygroscopic, which has a significant influence on their properties and applications. On the one side, the sorption of water induces a dramatic change in the properties of AcILs. On the other side, AcILs can be used as drying mate-

rials since they have high hygroscopicity. These two sides seem to be contradictory, but might lead to a development in harmony with each other if undertaken properly.

3.1 High Hygroscopicity

The hygroscopicity was determined by exposing the AcILs to air for 40 h, at an average temperature (T) of 25.3°C ($\delta_T = 0.18^\circ\text{C}$) and an average RH of 35.3 % ($\delta_{\text{RH}} = 0.17\%$) (Fig. 1). Directly exposing AcILs to moisture to test their hygroscopicity is a fast and practical approach, despite the less favorable reproducibility. Fig. 2 shows that AcILs are highly hygroscopic. Among the five AcILs investigated, [EMIM][Ac] absorbs the highest amount of water and [OMIM][Ac] absorbs the lowest amount (Fig. 2). The order of hygroscopicity is: [EMIM][Ac] > [BMMIM][Ac] > [BMIM][Ac] > [HMIM][Ac] > [OMIM][Ac] (Fig. 2). Their water sorption capacities within 40 h are 23.58, 20.40, 17.55, 13.86, and 14.65 % $\text{H}_2\text{O}/\text{IL}$, respectively. Note that in a previous report [BMIM][Ac] absorbed 15.36 % $\text{H}_2\text{O}/\text{IL}$ within 3 h at 23°C and 52 % RH. When compared to the result obtained here, even though the RH (35.3 %) is lower than in the earlier report (52 %), the water sorption capacity is higher than before, because of the longer time and the relatively higher temperature. Also, all the AcILs absorb water from air quickly at first, then slower, indicating a decreasing rate for the increase in water sorption capacity.

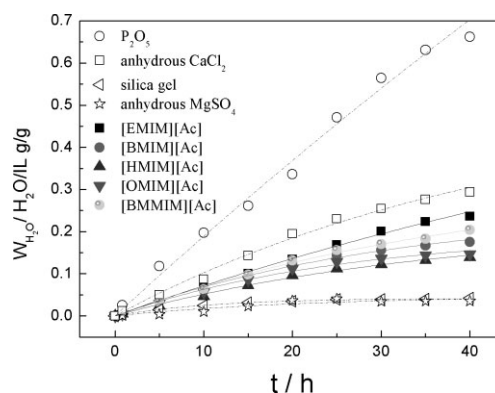


Figure 2. Hygroscopicity of AcILs exposed to the moisture in air at the average values $\mu_T = 25.3^\circ\text{C}$ and $\mu_{\text{RH}} = 35.3\%$ within 40 h.

Another interesting finding is that the AcILs with C2-methylation ([BMMIM][Ac]) is more hygroscopic than the non-C2-methylation counterpart ([BMIM][Ac]) (Fig. 2). This seems to indicate that the water-[BMMIM][Ac] interaction is stronger than that of water-[BMIM][Ac]. However, other researchers reported that water had a higher affinity to the C2H, i.e., a greater interaction (mainly hydrogen bonding) with [BMIM][Ac] [43]. This indicates that the water-[BMMIM][Ac] interaction is mainly entropy driven rather than through hydrogen bonding. Hunt [44] also found that the loss in entropy for [BMMIM][Cl] outweighs the loss in hydrogen bonding between $[\text{BMMIM}]^+$ and $[\text{Cl}]^-$. Therefore, the C2-methylation ILs, i.e., [BMMIM][Ac], might create more free volume than

the non-C2-methylation counterpart, i.e. [BMIM][Ac], thus allowing water to attack [BMMIM][Ac] more easily [26].

The hygroscopicity of AcILs could also be corroborated by the IR spectra after their exposure to air. The ν_{OH} of the IR

absorbance increases with time (Fig. 3), indicating that water sorption occurs [32]. The ν_{OH} absorbance follows the order [EMIM][Ac] > [BMMIM][Ac] > [BMIM][Ac] > [HMIM][Ac] > [OMIM][Ac], i.e. the same as with the water sorption capa-

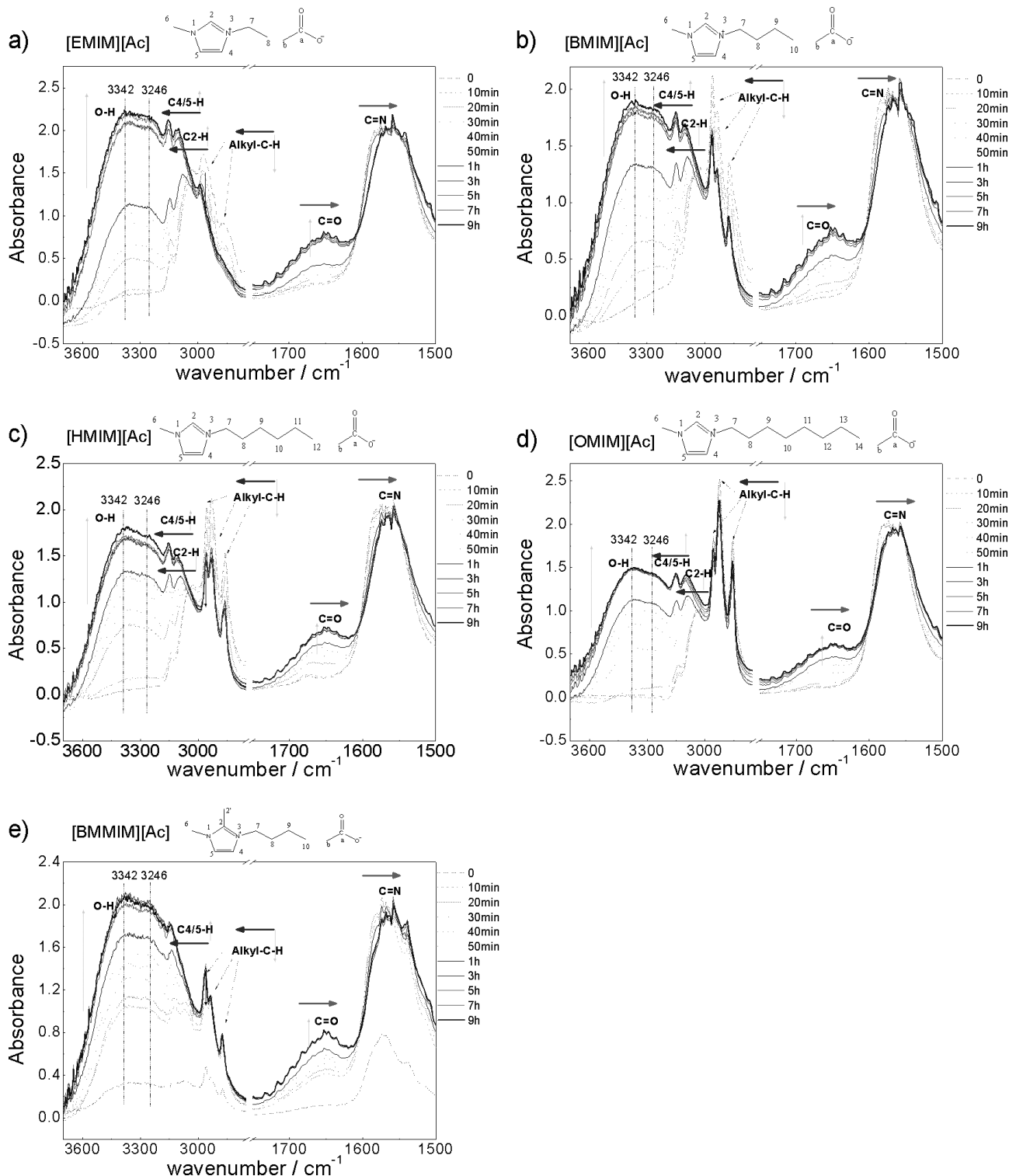


Figure 3. IR spectra of the AcIL–H₂O systems exposed to air with time: (a) [EMIM][Ac], (b) [BMIM][Ac], (c) [HMIM][Ac], (d) [OMIM][Ac], (e) [BMMIM][Ac].

city. In addition, the increase rate of the ν_{OH} absorbance decreases with time, also in good agreement with that of the water sorption capacity. In other words, the ν_{OH} of the IR absorbance is a qualitative indicator of the water sorption capacity and rate. Results of quantifying the water content in ILs by IR spectroscopy were also available [45].

The hygroscopicity kinetics of AClILs was also investigated by the modified two-step water sorption model, $W = W_{\infty}(1 - e^{-kt})$ [28]. The three kinds of hygroscopicity parameters, i.e., sorption capacity, sorption rate, and degree of difficulty to reach equilibrium, derived from the above model are shown in Tab. 2. The hydrophilicity of ILs (HPI), indicated by the steady-state water sorption capacity $100W_{\infty}$ is also a parameter to indicate the interaction between ILs and water [28]. HPI is classified into four levels by $100W_{\infty}$, i.e., level 1: super-high hydrophilicity ($15 \leq \text{HPI}$); level 2: high hydrophilicity ($7.5 \leq \text{HPI} < 15$); level 3: medium hydrophilicity ($2.5 \leq \text{HPI} < 7.5$); and level 4: low hydrophilicity ($0 \leq \text{HPI} < 2.5$) [28]. According to this criterion, all the AClILs investigated have super-high hydrophilicity (Fig. 4). Compared with our previous investigations, ILs with the anion Ac are the only category of ILs with all their derivatives in the highest level of hydrophilicity at a similar temperature and RH [28, 29].

This high hygroscopicity of AClILs has a significant influence on the applications of AClILs, which are described below.

3.2 Influence on Physical Properties

The presence of water caused by high hygroscopicity has a dramatical influence on the properties of AClILs. Fig. 5 shows that the viscosity of [OMIM][Ac] reduces to about one-fifth after mixing with only $10 \text{ g g}^{-1} \text{ H}_2\text{O/IL}$. If [OMIM][Ac] is saturated with water (i.e. $14.65 \text{ g g}^{-1} \text{ H}_2\text{O/IL}$) by exposure to air under the

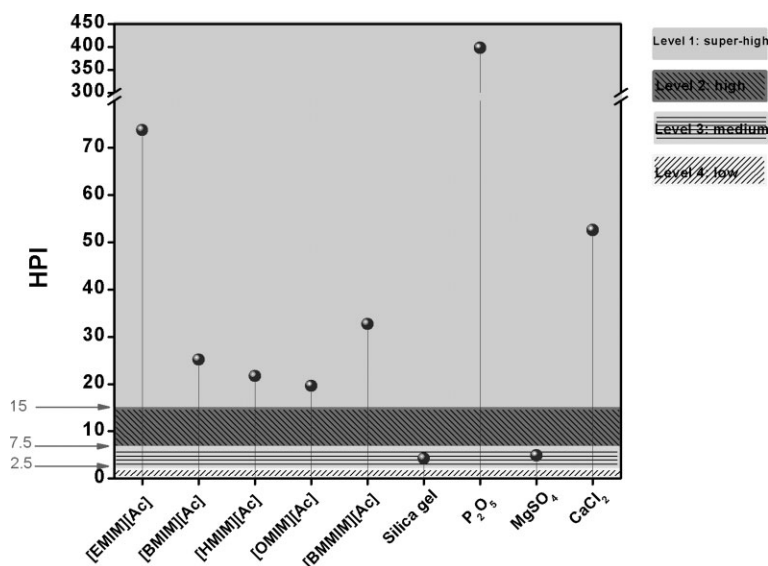


Figure 4. Four levels of hydrophilicity (HPI) of AClILs indicated by the steady-state water absorption capacity $100W_{\infty}$ derived from the modified two-step sorption model [28].

conditions investigated, the viscosity would decrease from cal. 900 mPa s to cal. 100 mPa s . The density of the AClILs also changes obviously (Fig. 6) with increasing water concentration. The turning points of the physical properties in Fig. 5 (cal. $0.05 \text{ g g}^{-1} \text{ H}_2\text{O/IL}$) and Fig. 6 (cal. 0.05 and $0.25 \text{ g g}^{-1} \text{ H}_2\text{O/IL}$) suggest a change in chemical structure of the AClIL- H_2O system. Zhang et al. [46] also witnessed two turning points (i.e., from a dimensional network to an ionic cluster, then to ionic pairs) of the ILs investigated ([EMIM][BF₄]) by two-dimensional correlation spectroscopy.

Moreover, ILs such as AClILs have ionic traits, which provide ILs with many favorable features, e.g., nonmeasurable volatility. Absorbing water from the ubiquitous moisture in air would make AClILs more molecular, i.e. reduce the ionicity of AClILs.

Table 2. Sorption capacities, degrees of difficulty to reach sorption equilibrium, and sorption rates of the investigated AClILs and other traditional drying materials.

No.	IL	Sorption capacity		Degree of difficulty to reach sorption equilibrium		Sorption rate		<i>R</i> ²
		$W_{40\text{h}}$ [%]	W_{∞} [%]	$1/k$ [h]	kW_{∞} [% h ⁻¹]	$R_{30\text{min}}$ [% h ⁻¹]	R^2	
1	[EMIM][Ac]	23.58	73.76	97.94	753.10	1.59	0.9974	
2	[BMIM][Ac]	17.55	25.16	31.37	802.23	1.06	0.9950	
3	[HMIM][Ac]	13.86	21.66	36.54	592.78	0.86	0.9938	
4	[OMIM][Ac]	14.65	19.63	25.76	761.84	0.54	0.9911	
5	[BMMIM][Ac]	20.40	32.69	40.90	799.25	1.00	0.9956	
6	Silica gel	4.24	4.22	10.99	383.49	0.40	0.9962	
7	P ₂ O ₅	66.19	397.83	205.76	1933.46	3.07	0.9921	
8	MgSO ₄	3.50	4.87	22.52	216.05	0.12	0.8854	
9	CaCl ₂	29.37	52.58	46.13	1139.89	1.66	0.9941	

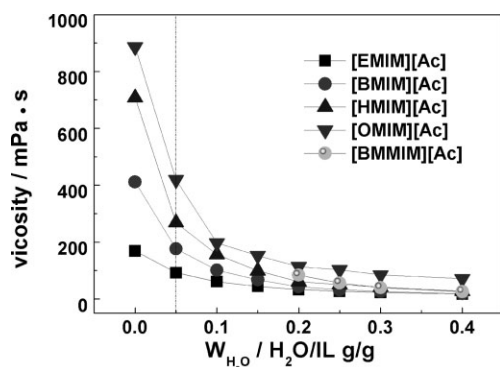


Figure 5. The viscosities of the AcIL–H₂O systems versus the water concentration. The dash-dot line points to the special concentration point of 0.25 g g^{−1} H₂O/IL.

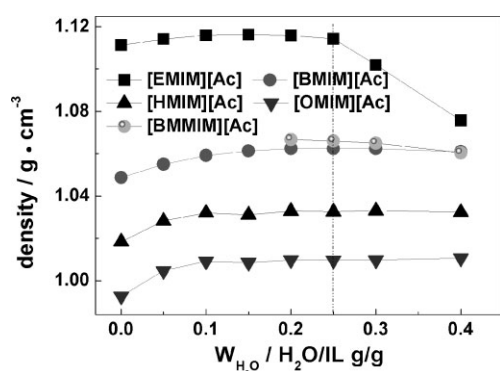


Figure 6. The densities of the AcIL–H₂O systems versus the water concentration. The dash-dot line points to the special concentration point of 0.25 g g^{−1} H₂O/IL.

The introduction of molecular characteristics might give ILs the features of a molecular liquid, such as high volatility and less stability. This might bring ILs back into the history of environmental-unfriendly VOC. In addition, water might also chemically interact with ILs, e.g., [BMIM][BF₄] and [BMIM][PF₆], to produce detrimental gaseous products [47]. Hydrogen-bonding interactions of ILs and water also change the structure and properties of ILs (including AcILs) [37, 48–52]. So many researchers suggested the synthesis of functionalized ILs to solve the drawbacks of mixing with a molecular liquid such as water [53].

The alterations in the physical properties of AcILs in the presence of water could also be verified by the change of their microscopic structure upon exposure to air, measured by ATR-IR (Fig. 3). The results show that $\nu_{\text{C}2\text{H}}$, $\nu_{\text{C}2'\text{H}}$, $\nu_{\text{C}4,5\text{H}}$ and $\nu_{\text{C}6,7,\text{xH}}$ (i.e. alkyl hydrogen) show a blue shift, ν_{OH} shows nearly no shift, while $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{C}=\text{O}}$ show a slight and obvious red shift (Fig. 3). The shifts of the IR spectra indicate a microscopic structural change of the AcILs in the presence of water; the physical properties are thus changed. Moreover, the obvious red shift of $\nu_{\text{C}=\text{O}}$ indicates that water mainly interacts with the C=O of the anion through hydrogen bonding. This result is consistent with other reports [26, 49, 54].

3.3 Potential Usage as Drying Materials

Fig. 2 shows that [EMIM][Ac] is the most hygroscopic (23.58 % H₂O/IL) ILs among the five AcILs investigated. It gives us a hint that it can be potentially used as drying material. Then the performance of [EMIM][Ac] as drying material was assessed compared with four conventional drying materials, i.e., P₂O₅, anhydrous CaCl₂, silica gel, and anhydrous MgSO₄. The results show that the hygroscopicity of [EMIM][Ac] is about three times lower than that of P₂O₅, similar to CaCl₂, and about five times greater than that of silica gel and MgSO₄ (Fig. 2).

The regeneration efficiencies of AcILs and other desiccants (P₂O₅, CaCl₂, and [EMIM][Ac]) were also tested four times. Desorption of water was conducted in vacuum at 70 °C for 20 h for each regeneration. After each of the four times of water desorption, the AcILs was exposed to air with the following average temperatures and pressures: (1st) $T = 25.1$ °C, $\delta_T = 1.0$ °C and RH = 34.4 %, $\delta_{\text{RH}} = 1.41$ %; (2nd) $T = 26.2$ °C, $\delta_T = 1.3$ °C and RH = 34.9 %, $\delta_{\text{RH}} = 1.23$ %; (3rd) $T = 21.1$ °C, $\delta_T = 1.3$ °C and RH = 30.4 %, $\delta_{\text{RH}} = 1.36$ %; (4th) $T = 20.1$ °C, $\delta_T = 1.1$ °C and RH = 33.38 %, $\delta_{\text{RH}} = 1.19$ %. The regeneration results indicate that [EMIM][Ac] could be regenerated four times without obvious efficiency loss. For example, after the first water desorption process, the water contents in the ILs remained as only 785 ppm, which can prove the relatively high regeneration efficiency of [EMIM][Ac]. In contrast, the regeneration efficiency of P₂O₅ is the least due to the chemical reaction with water.

From the point of view of water sorption capacity, P₂O₅ is preferred as drying materials over ILs, including AcILs, because of the higher water sorption capacity and rate compared to AcILs (Fig. 2, Tab. 2). In terms of hydrophilicity (HPI), P₂O₅ is also more hydrophilic than AcILs, even within the same HPI range (Fig. 4). In practice, P₂O₅ is usually used to dry ILs, including AcILs in a vacuum oven, which has often been reported in the literature [55]. However, the water absorption process of P₂O₅ is irreversible under normal conditions, due to the chemical reaction with water; some unexpected toxic gases, e.g., *meta*-phosphoric acid (HPO₃), may also be produced. When considering the recyclability of P₂O₅ and [EMIM][Ac], this may hint at the potential use of the hygroscopic ILs, e.g., [EMIM][Ac], as drying materials, although [EMIM][Ac] is less hygroscopic.

Actually, in addition to P₂O₅, we also used CaCl₂ to dry substances. Bearing in mind that the hygroscopicity and regeneration of [EMIM][Ac] are comparable to those of CaCl₂, we can also use [EMIM][Ac] as drying material. Theoretically, there are as much as 10¹⁸ ILs, and the synthesis of more hygroscopic ILs as drying materials is expected. Moreover, the tunable ILs can be used as drying materials in situations when the use of CaCl₂ is impracticable, such as in drying C₂H₅OH or NH₃, because CaCl₂ can interact with C₂H₅OH and NH₃ to produce CaCl₂ × 4C₂H₅OH and CaCl₂ × 8NH₃, respectively. In short, the high hygroscopicity, the favorable regeneration, the negligible volatility, and the flexible tunability all contribute to the potential usage of AcILs as drying materials.

4 Conclusion

AcILs were found to be very hygroscopic. This hygroscopicity has both positive and negative influences on AcILs. It is better to make full use of those two effects, refraining from the unintended to get the intended or turning the disfavored into the favored. The potential use of AcILs, especially [EMIM][Ac], as drying materials could be very useful due to their favorable regeneration, high capacity, and desirable biodegradability. More IL candidates, particularly functionalized ILs, could be designed as drying materials because of the high tunability of ILs.

Note that AcILs applied as drying materials are just a prototype. We made the conclusion in an indirect way, i.e. by comparison of the hygroscopicities between AcILs and traditional drying materials, rather than in a direct way. More work needs to be done for the industrial application of ILs, particularly AcILs, as drying materials.

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Symbols used

$1/k$	[h]	degree of difficulty to reach equilibrium
kW_{∞}	$[\% \text{ h}^{-1}]$	initial rate of water sorption
R^2	[-]	adjusted R squared
$R_{30\text{min}}$	$[\% \text{ h}^{-1}]$	average rate of water sorption
RH	[%]	relative humidity
T	$^{\circ}\text{C}$	temperature
$W_{40\text{h}}$	[%]	water sorption capacity within 40 h
W_{∞}	[%]	steady-state saturated water sorption capacity

Greek symbols

δ_{RH}	[%]	standard deviation of the relative humidity
δ_{T}	$^{\circ}\text{C}$	standard deviation of the temperature
μ_{RH}	[%]	mean value of the relative humidity
μ_{T}	$^{\circ}\text{C}$	mean value of the temperature

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