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A Comparative Study on Absorption and Selectivity of Organic Vapors by Using Ionic Liquids Based on Imidazolium, Quaternary Ammonium, and Guanidinium Cations

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Abstract: A novel study on organic solute absorption from the vapor phase is reported. The organic solutes chosen for the absorption studies include 1,4-benzodioxane, biphenyl, xanthene, and menthol. A series of imidazolium, ammonium, and guanidinium-based ionic liquids (ILs) containing several types of anions were used as absorbents. Absorption of water vapor was also studied along with the organic solutes. Absorption studies of each organic solute were performed by using a specially devised glass apparatus at 50 °C. It was observed that the rate of absorption increases with time and is faster in the case of 1,4-benzodioxane (24 h). The absorption process for each organic solute with different classes of ionic liquids was studied and the results were compared with each other. Absorption values of more than 25 000 ppm were observed in some ionic liquids. Distribution ratios of organic solutes in an ionic liquid and in the vapor phase were measured and the selectivity was evaluated by using the distribution ratio values. A remarkable selectivity was observed for some ionic liquids towards a specific organic solute. Importantly, it was observed that the selectivity remained constant, even though a mixture of solute was used for the absorption study. Desorption of organic vapors from ionic liquids was successfully carried out by applying a vacuum. Further, it was observed that the same ionic liquid can be repeatedly reused several times for absorption. These studies reveal that, in future, a task-specific ionic liquid can be prepared and used for specific solute capture from the vapor phase.

Keywords: absorption • desorption • ionic liquids • organic vapors • selectivity

Introduction

Ionic liquids (ILs) are a class of organic salts that exist as liquids at temperatures lower than 100 °C.[1–4] A significant characteristic of ionic liquids is their immensely low vapor pressure.[5,6] Many ionic liquids are regarded as green solvents mainly because they do not contaminate the atmosphere, contrary to conventional volatile organic compounds (VOC).[7] They can be hydrophilic or hydrophobic, depending on the structures of cations and anions. Ionic liquids exhibit various attractive properties, such as good chemical and thermal stability, nonflammability, high ionic conductivity, and a large electrochemical window. Therefore, they have been extensively investigated as solvents or co-catalysts in many more environmentally friendly chemical[5,8,9] and separation processes,[10–12] such as extraction with organic solvents and $scCO_2$,[13,14] pervaporation,[15] and extraction with supported liquid membranes.[16,17]

Recently, CO_2 and SO_2 were found to be extremely soluble in ionic liquids and hence the uses of ionic liquids as nonvolatile and reversible absorbents for the separation of CO_2 and SO_2 have been explored.[18–24] It was observed that the solubility of these gases were largely dependent on the structures of cation and anion used.[25,26] Ionic liquids were also immobilized in the supported liquid membranes and used for CO_2 absorption.[27] These membranes containing ionic liquids offered higher permeation and selectivity and could be used several times as there is no loss of solvent. However, the application of an ionic liquid as an absorbent material is limited to these gases only and, to the best of our knowledge, nothing has been reported about their possible application in the capture of other vapor streams.

In our effort to explore new applications of ionic liquids in the absorption process, we observed that some organic

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solutes can also be removed successfully from the vapor phase. The organic solutes chosen for the absorption studies include 1,4-benzodioxane, biphenyl, xanthene, and menthol. In this study, our basic intention was to utilize the advantage of the thermal stability of ionic liquids and to examine whether they have any affinity for the organic solutes other than the typical CO_2 and SO_2 gases. Herein, the solutes were chosen such that they represent different categories, such as contaminant, endocrine disruptor, fungicide, and fragrance, respectively.[28,29] These solutes may present in the atmosphere in the gaseous state.

A simulated vapor stream of each solute was generated by using an oil bath at constant temperature. Several types of ionic liquids involving a combination of cations based on imidazolium, ammonium, and guanidinium with readily available anions were prepared and characterized, such as the cations, 1-benzyl-3-methylimidazolium $[Bzmim]^+$, 1,3-dibenzylimidazolium $[BzimBz]^+$, 1-octyl-3-methylimidazolium $[C_8mim]^+$, 1-decyl-3-methylimidazolium $[C_{10}mim]^+$, tricaprylmethylammonium $[Aliquat]^+$, benzyltriethylammonium $[BzTEA]^+$, phenyltrimethylammonium $[PhTMA]^+$, and dimethyldihexylguanidinium $[DMG]^+$ and the anions, *p*-toluene sulfonate $[TSA]^-$, dicyanoamide $[DCA]^-$, saccharine (2-sulfobenzoic acid imide sodium salt) $[SAC]^-$, trifluoroacetate $[TFA]^-$, bis(trifluoromethanesulfonyl)imide $[Tf_2N]^-$, trifluoromethanesulfonate $[TfO]^-$, and thiocyanate $[SCN]^-$. Here, their application in the absorption of selected organic solutes is reported. The absorption of water vapors is also studied in order to disclose the most hydrophobic combination of cations and anions. The absorption and desorption behavior of organic solutes in the ionic liquids was studied. In case of the aromatic compounds, their absorption selectivities were compared with each other.

Results and Discussion

Absorption kinetics: The absorption studies of each organic solute were performed in a specially devised glass apparatus (see Supporting Information). Absorption runs were carried out by using 2 g of the organic solute and 0.1 g of the ionic liquid. A stream of organic vapors was generated by using a 50 °C temperature and an air flow of $15\,cm^3\,min^{-1}$. Initially, absorption kinetics for individual organic solutes were studied by selecting [Aliquat][DCA] as an absorbent. Figure 1 exhibits the rate of absorption of organic solute in [Aliquat][DCA]. The amount of organic solute absorbed increases with time until equilibrium, which is reached for each solute within 24 to 48 h. From this figure, it can be concluded that the rate of absorption of 1,4-benzodioxane is faster than biphenyl, xanthene, and menthol. Xanthene presents the longest equilibrium time of 48 h. The difference in the rates of absorption for the organic solutes at same temperature is due to their differing physical properties.

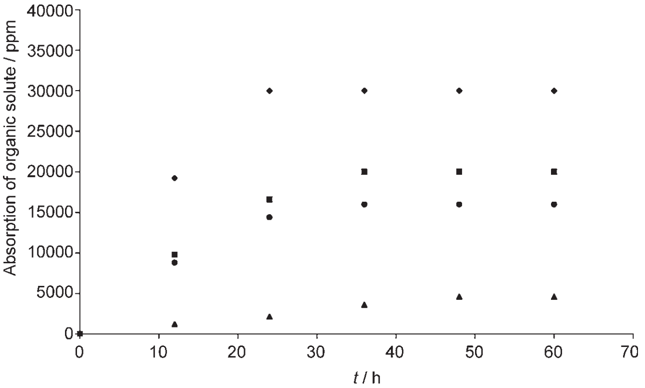

Figure 1. Absorption of 1,4-benzodioxane ◆, biphenyl ■, xanthene ▲, and menthol ● by [Aliquat][DCA] as a function of time (ppm = µg of organic vapor per g of ionic liquid).

At equilibrium, the concentration of each compound in the ionic liquid, [Aliquat][DCA], was found to be $30\times10^3\,\mu g\,g^{-1}$ ($33\times10^3\,\mu g\,mL^{-1}$) of 1,4-benzodioxane, $20\times10^3\,\mu g\,g^{-1}$ ($22\times10^3\,\mu g\,mL^{-1}$) of biphenyl, $4.6\times10^3\,\mu g\,g^{-1}$ ($5.1\times10^3\,\mu g\,mL^{-1}$) of xanthene, and $16\times10^3\,\mu g\,g^{-1}$ ($17.7\times10^3\,\mu g\,mL^{-1}$) of menthol. The vapor phase concentrations of 1,4-benzodioxane, biphenyl, xanthene, and menthol were 0.7, 0.3, 0.13 and $1\,\mu g\,mL^{-1}$, respectively. This impressive increase of concentration in the ionic liquids in relation to the vapor phase achieved in one equilibrium stage clearly demonstrates the enormous potential of this media for efficient removal of organic solutes present at low concentrations ($<1\,\mu g\,mL^{-1}$).

To establish some information about the chemical interaction between the organic solute and the ionic liquid, we characterized the vapor-free and vapor-treated ionic liquid by NMR and FTIR spectroscopy by using the biphenyl–[Aliquat][DCA] system. The ^1H NMR spectra of the biphenyl-treated and untreated [Aliquat][DCA] are presented in Figure 2. As expected, three new resonances were observed at $\delta = 7.56$ (doublet, 4H), 7.4 (triplet, 4H), and 7.32 ppm (triplet, 4H), which indicates the presence of the biphenyl ring. Similarly, FTIR spectra of the biphenyl-absorbed [Aliquat][DCA] and biphenyl-free [Aliquat][DCA] showed only the new additional absorption bands characteristic of biphenyl alone. These observations suggest that there is no considerable specific bond formed between the [Aliquat][DCA] and biphenyl during the absorption and probably the absorption of organic vapor in the ionic liquids is mainly physical and governed by weak van der Waals forces of attraction.

Absorption by using an imidazolium class of ionic liquids: The absorption of individual organic solutes in the imidazolium ionic liquids was studied and some representative examples are shown in Figure 3a and b. The absorption run was carried out at 50 °C for 48 h in order to attain equilibrium amongst all the solutes. Initially, the effect of the anion on the absorption process of organic solutes was studied. For this purpose, cation $[Bzmim]^+$ was used and the anions were varied which included, $[TSA]^-$, $[DCA]^-$, $[SAC]^-$, $[TFA]^-$, $[Tf_2N]^-$, and $[TfO]^-$. The results illustrate that, in general, 1,4-benzodioxane has a strong affinity for all the

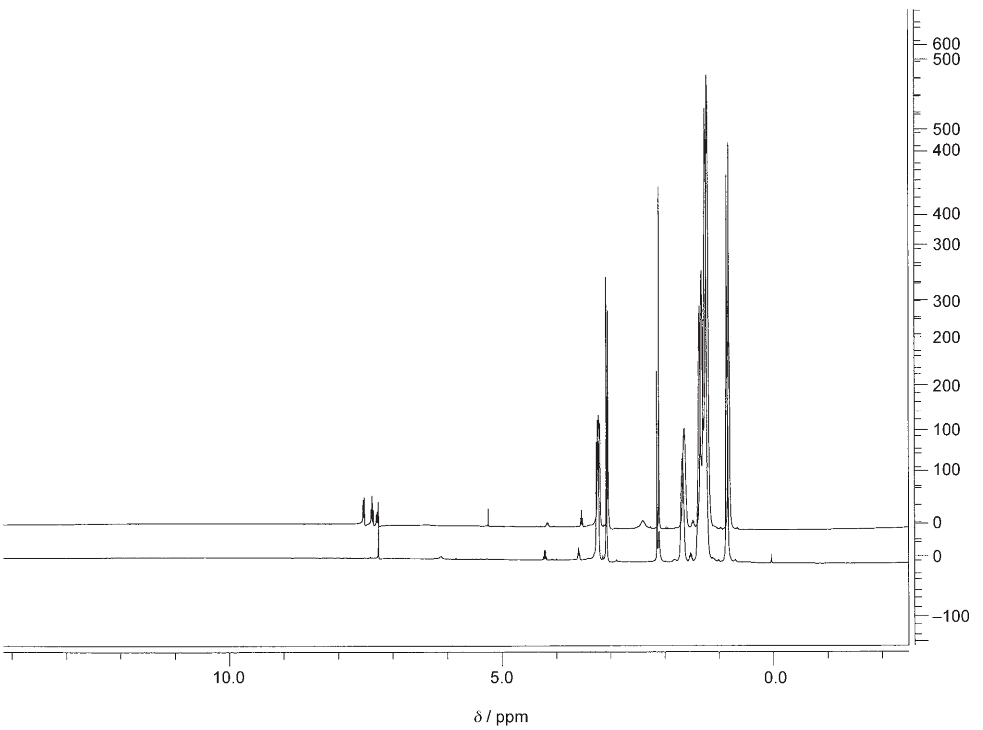

Figure 2. ^1H NMR spectra (400 MHz) of the [Aliquat][DCA] (bottom spectrum) and biphenyl-absorbed [Aliquat][DCA] (upper spectrum) in $CDCl_3$.

[Bzmim] classes of ionic liquids. However, the highest absorption capacity of 24300 ppm was observed in the case of organic solute menthol and for [Bzmim][DCA]. Absorption of biphenyl and xanthene was also observed to be good in the ionic liquid [Bzmim][DCA] compared to the other ionic liquids. Therefore, it has shown excellent absorption capacity for the present organic solutes. However, [Bzmim][TfO] and [Bzmim][SAC] were found to be poor absorbing agents.

The above findings revealed that $[DCA]^-$ is one of the best anions in comparison with the other anions studied, which may be due to its strong basicity thereby causing more absorption of organic solutes in the bulk. Therefore, further studies were planned by keeping the anion $[DCA]^-$ constant and varying the imidazolium cation. The other two imidazolium cations used were $[BzimBz]^+$ and $[C_8mim]^+$. Figure 3b shows that the replacement of the methyl group by the aromatic benzyl group decreases the absorption of organic solutes while the replacement of the methyl group with the long alkyl chain molecule increases the absorption capacity of ionic liquids. The lowest value of absorption of 900 ppm was found in xanthene–[BzimBz][DCA].

Absorption by using ammonium ionic liquids: The effect of the ammonium class of ionic liquids on the absorption process was studied by using the Aliquat series of ionic liquids. Figure 4a illustrates that, in general (with the exception of [Aliquat][TSA]), when the imidazolium cation $[Bzmim]^+$ is replaced by $[Aliquat]^+$, efficiency of absorption of all the organic solutes is increased. The aliquat containing the $[DCA]^-$ anion showed a remarkable absorption capacity. In particular, 1,4-benzodioxane has shown a maximum absorption capacity of 29600 ppm which was 17000 ppm in [Bzmim][DCA]. One of the important findings of this study also shows that [Aliquat][TSA] has not shown any affinity for the xanthene.

The effect of the cation in the ammonium series was also studied. For this purpose, anion $[TFA]^-$ was kept constant while the cations were varied (Figure 4b). The effect shows that the absorption capacity of organic solutes decreases as follows: $[Aliquat]^+ > [BzTEA]^+ > [PhTMA]^+$. This decrease is several times lower, for instance absorption of menthol in [Aliquat][TFA] is 17230 ppm and in [PhTMA][TFA] only 200 ppm. This shows that the ammonium ionic liquids which are completely devoid of aromatic groups result in the highest absorption efficiency; this is followed by ionic liquids which contain benzyl groups in which the aromatic ring is not directly attached to the nitrogen atom and then ionic liquids which contain the phenyl ring which is directly attached to the nitrogen. The presence of the aromatic ring in the $[PhTMA]^+$ and $[BzTEA]^+$ cations should in principle allow an extra absorption capability due to the possibility of the formation of π–π interactions. However, the observed opposite results also observed in the case of the imidazolium series demonstrates that this is not the relevant interaction. Probably the combination of an organized three-dimensional network structure of the ionic liquid with the capability of the solute being integrated inside plays an important role.

Comparison of absorption between imidazolium, ammonium, and guanidinium classes of ionic liquids: The foregoing studies have prompted us to study the absorption behavior of organic solutes by using one more class of ionic liquids, the guanidinium class. In this case, it was decided to compare the results of imidazolium and ammonium compounds with the guanidinium class of ionic liquids. Therefore ionic liquids $[DMG][Tf_2N]$, $[Aliquat][Tf_2N]$, and $[Bzmim][Tf_2N]$ were selected. The results were shown in Figure 5, which demonstrates that the absorption capacities of the guanidinium compounds are similar to the imidazolium ionic liquids but lower than the ammonium ionic liquid $[Aliquat][Tf_2N]$.

Absorption of water by using ionic liquids: Ionic liquids being hygroscopic in nature can absorb a significant amount

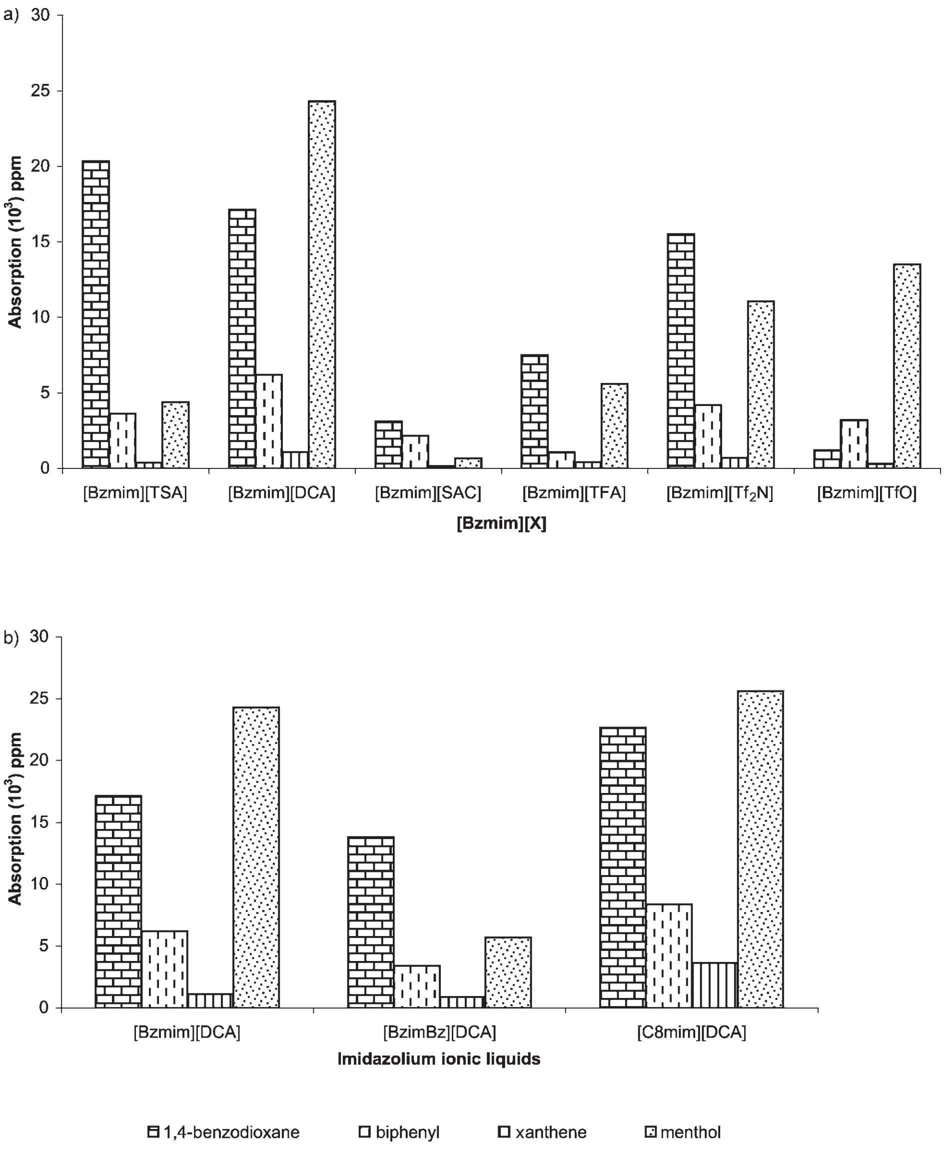

Figure 3. Comparative absorption of 1,4-benzodioxane, biphenyl, xanthene, and menthol by ionic liquids containing a) the [Bzmim]$^+$ cation and several anions and b) the [DCA]$^-$ anion and several cations (ppm = µg of organic vapor per g of ionic liquid).

of water. Their physicochemical properties are not only changed by, but also are dependent on the amount of absorbed water.[30–32] In addition, efficiencies of various chemical processes in ionic liquids are dependent on absorbed water. Herein, we report our studies related with the water-vapor absorption by using ionic liquids. In this instance, vapor was generated at 50 °C and absorption in various ionic liquids were tested over 48 h. Initial $[(H_2O)]_i$ and final $[(H_2O)]_f$ water contents in the ionic liquid were measured and the difference between them gave the true water vapor absorption values (Table 1). In the imidazolium series, the absorption of water vapor was found to be increased with the substitution of the methyl group by aromatic ring and long alkyl chain. In this series, it was found that the [Bzmim]$^+$ cation has the least tendency to absorb water vapors, which was followed by [BzimBz]$^+$ and [C$_8$mim]$^+$ cations. In the same series, the tendency of the anion to absorb the water vapor decreases as follows: [TFA]$^-$ > [SAC]$^-$ > [DCA]$^-$ > [TfO]$^-$ > [Tf$_2$N]$^-$. Amongst the ammonium group, the absorption of water vapor has not shown any specific trend. More interestingly, it was observed that the water vapor absorption by guanidinium cations was far less than the imidazolium and ammonium cations. These cations seem to be less hydrophobic and can have wide applications in the chemical processes, for example, the absorption of water vapor by [DMG][Tf$_2$N] is only 0.04 µg mg^{-1}. The anions a have major impact on the absorption process, the values indicated in Table 1 show that the ionic liquids containing the [TFA]$^-$ anion have very high absorption values (> 12 µg mg^{-1}) and the highest is [Aliquat][TFA]. These observations are similar to the data presented by Cammarata et al.[33]

Distribution ratio and selectivity: The distribution ratio (enrichment factor) for each organic solute was calculated by using the ratio of concentration of gas in the ionic liquid to the concentration of gas in the vapor phase (air). Extremely high distribution ratios in the order of 10^3 to 10^4 may be achieved when using appropriate combinations of ionic liquid and organic solute.

The selectivity of each organic solute towards every ionic liquid was calculated by using ratios of individual distribution ratios. It is interesting to observe how the selectivity depends on the structure of the different ionic liquids. In the case of biphenyl versus xanthene, the absorption selectivity changed from 5.69 to 0.52, respectively, when using [Bzmim][SAC] and [C$_8$mim][TFA] (Table 2). These findings are extremely interesting because they demonstrate how the design and selection of an optimized ionic liquid structure can determine the preferential absorption of a given organic solute from a vapor phase.

Under real operating conditions, the contaminated air stream will contain different organic vapors. Hence, it is very important that the individual absorption capability is

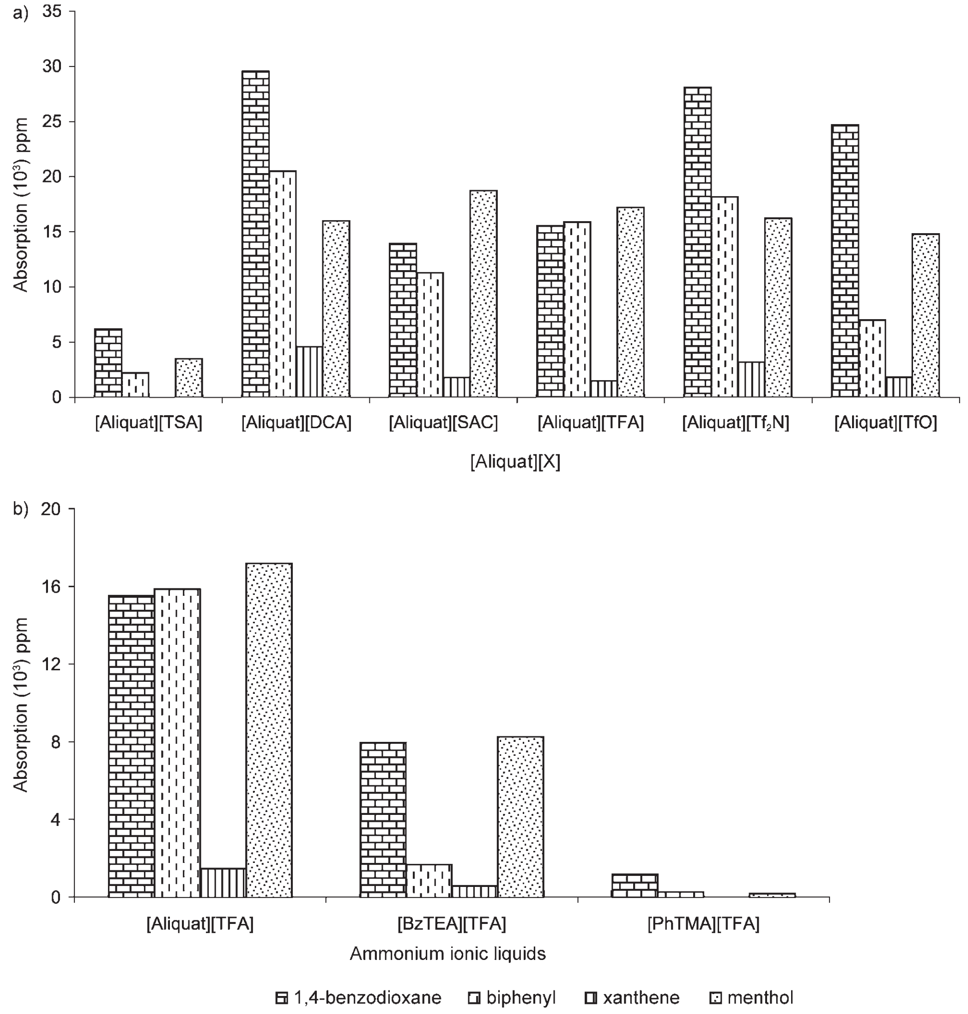

Figure 4. Comparative absorption of 1,4-benzodioxane, biphenyl, xanthene, and menthol by an ionic liquid containing a) the [Aliquat]$^+$ cation and several anions and b) the [TFA]$^-$ anion and several cations (ppm = µg of organic vapor per g of ionic liquid).

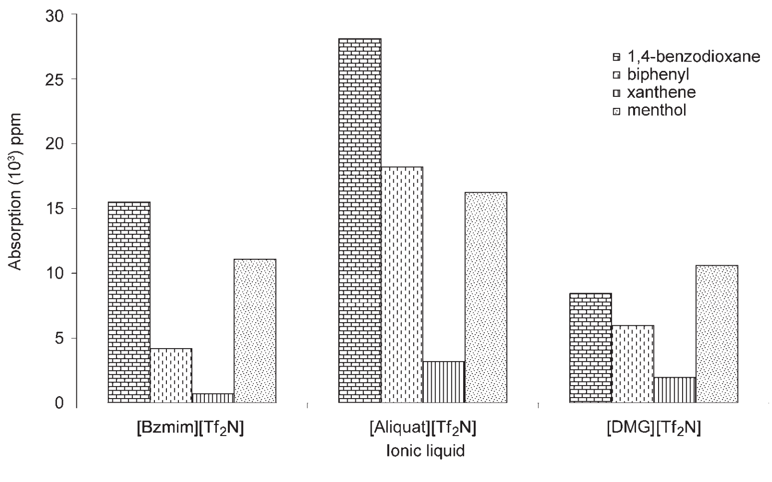

Figure 5. Comparative absorption of 1,4-benzodioxane, biphenyl, xanthene, and menthol by an ionic liquid containing the [Tf$_2$N]$^-$ anion and [Bzmim]$^+$, [Aliquat]$^+$, and [DMG]$^+$ cations (ppm = µg of organic vapor per g of ionic liquid).

retained. In order to assess this problem, the selectivity of 1,4-benzodioxane versus biphenyl was determined by placing these two compounds in the same chamber at the same temperature (50 °C). Ionic liquids such as, [Bzmim][SAC], [C$_8$mim][DCA], and [C$_8$mim][SAC] were used for this particular study. Fortunately, it was found that the selectivity remains constant for the given organic solute and ionic liquid, when compared to the previous monocomponent experiments. Figures 6, 7, and 8 show the chromatographs of 1,4-benzodioxane and biphenyl obtained during the mixture analysis.

Desorption and reusability of ionic liquids: The possibility to recover and concentrate the organic solutes back from the ionic liquids is also an important issue for the success of an overall process of organics removal and recovery. As expected, the organic solutes were successfully recovered from the ionic liquids by desorption under vacuum. The recovered organics can then be captured and concentrated by condensation of this stream. Compared to the absorption process, the desorption process is very fast and takes only 12 h for the complete desorption of organic vapors from ionic liquids.

A stable absorption capacity after repeated absorption and desorption is important for ionic liquids used for organic vapor absorption. Three cycles of repeated experiments of absorption and desorption were performed by using the biphenyl and [Aliquat][DCA] system. The desorbed ionic liquid [Aliquat][DCA] was tested repeatedly by putting it into a glass chamber containing vapors of biphenyl. Impor-

Table 1. Absorption of water by ionic liquids over 48 h.[a]

Ionic liquids	Initial water content $[(H_2O)]_i$	Final water content $[(H_2O)]_f$	Absorption $[(H_2O)_f-(H_2O)_i]$	Absorption ratio $[(H_2O)_f/(H_2O)_i]$
[Bzmim][DCA]	14.6	19.7	5.1	1.34
[Bzmim][SAC]	14.8	20.1	5.3	1.35
[Bzmim][TFA]	20.5	40.7	20.2	1.98
[Bzmim][Tf_2N]	5.7	6.6	0.9	1.15
[BzimBz][DCA]	6.5	12.9	6.4	1.98
[BzimBz][Tf_2N]	5.4	13.2	7.8	2.44
[C_8mim][DCA]	11.1	25.9	14.8	2.33
[C_8mim][SAC]	13.3	29.3	16.0	2.20
[C_8mim][TFA]	19.1	44.2	25.1	2.31
[C_8mim][Tf_2N]	5.8	8.9	3.1	1.53
[C_8mim][TfO]	4.5	8.5	4.0	1.88
[Aliquat][DCA]	2.9	6.0	3.1	2.06
[Aliquat][SAC]	2.3	5.7	3.4	2.47
[Aliquat][TFA]	7.7	36.8	29.1	4.77
[Aliquat][Tf_2N]	2.2	15.59	13.4	7.08
[BzTEA][TFA]	24	36.2	12.2	1.50
[PhTMA][TFA]	20.6	33	12.4	1.60
[DMG][TFA]	5.0	17.93	12.9	3.58
[DMG][Tf_2N]	6.4	6.44	0.04	1.00

[a] Values in μg (H_2O) mg^{-1} (IL) only.

Table 2. Selectivity of 1,4-benzodioxane versus biphenyl versus xanthene in different ionic liquids.

Ionic liquid	Selectivity[a] 1,4-benzodioxane/biphenyl	biphenyl/xanthene	1,4-benzodioxane/xanthene
[Bzmim][DCA]	1.18	2.46	2.92
[Bzmim][SAC]	0.62 (0.64)[b]	5.69	3.70
[Bzmim][TFA]	3.0	1.10	3.31
[C_8mim][DCA]	1.15 (1.15)[b]	1.0	1.16
[C_8mim][SAC]	1.16 (1.17)[b]	0.95	1.11
[C_8mim][TFA]	2.60	0.52	1.35
[Aliquat][DCA]	0.61	1.93	1.19
[Aliquat][SAC]	0.52	2.72	1.43
[Aliquat][TFA]	0.41	4.38	1.83
[Aliquat][TfO]	1.5	1.65	2.51
[DMG][Tf_2N]	0.59	1.36	0.80
[DMG][TfO]	0.77	4.10	3.17

[a] Determined on basis of individual distribution ratios. [b] Observed selectivity based on absorption from an air stream containing a mixture of 1,4-benzodioxane and biphenyl (distribution ratios or enrichment factor = concentration of solute in the ionic liquid at equilibrium ($\mu g\,g^{-1}$; density of ionic liquids is in the range of 0.85 to 1.45) to the concentration of solute in the vapor phase ($\mu g\,mL^{-1}$)).

tantly, the absorption (1st 22×10^3, 2nd 22×10^3, and 3rd 22×10^3 $\mu g\,mL^{-1}$) and desorption (1st 99.3, 2nd 99.0, 3rd 99.2%) capabilities were retained for the maximum three cycles tested by using the same sample of ionic liquid.

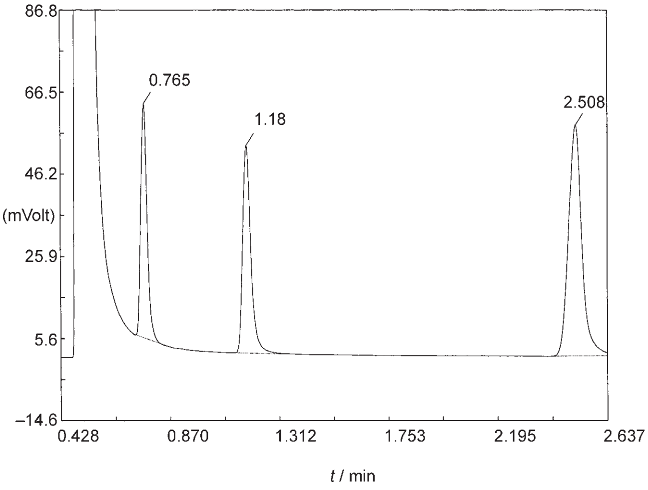

Figure 6. Gas chromatogram resulting from absorption from an air stream containing a mixture of 1,4-benzodioxane and biphenyl by [Bzmim][SAC]. $t_R = 0.77$ min (1,4-benzodioxane), $t_R = 1.18$ min (biphenyl), and $t_R = 2.51$ min (benzophenone, standard).

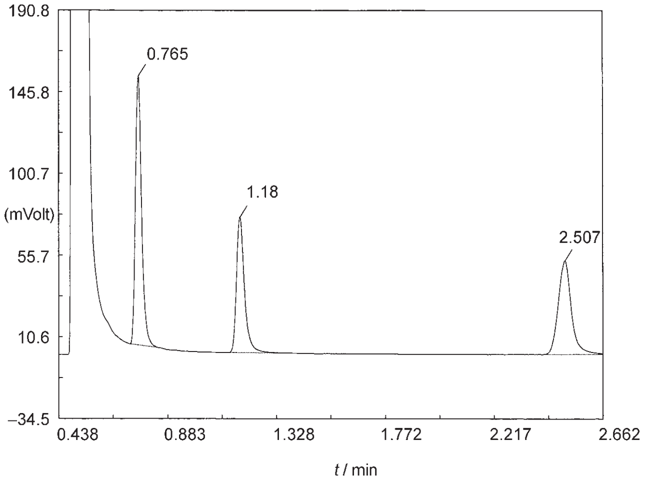

Figure 7. Gas chromatogram resulting from absorption from an air stream containing a mixture of 1,4-benzodioxane and biphenyl by [C_8mim][DCA].

Conclusion

These studies demonstrate the feasibility of using ionic liquids as absorbents for the selective absorption of solutes. Systematic experiments were performed with individual as well as different mixtures of organic solute and representative ionic liquids. From these experiments, we conclude that the appropriate combination of ionic liquid is crucial for achieving good selectivity in a given separation problem. The ammonium ionic liquids which are easy to prepare have the best absorption capacities. The high selectivity obtained in this work for the separation of mixtures of organic solute demonstrates the potential for the use of this methodology for the separation of a selected solute from complex mixtures. The emergence of a considerable number of thermally stable ionic liquids allows one to obtain the desired selectivity for a specific substrate mixture. A task-specific ionic liquid can be prepared for the best selectivity. To the best of our knowledge, the absorption process of organic vapors by using ionic liquids has never been tested. Within this context, we believe our results are of particular significance in

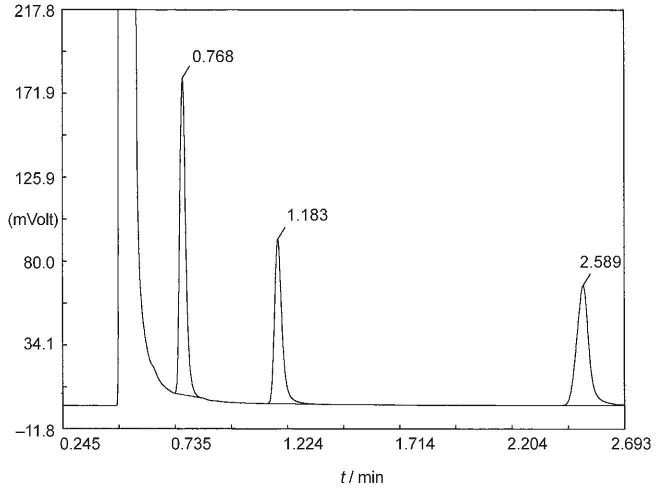

Figure 8. Gas chromatogram resulting from absorption from an air stream containing a mixture of 1,4-benzodioxane and biphenyl by [C$_8$mim][SAC].

establishing that ionic liquids can be designed for the processing of gases other than CO_2 and SO_2. Therefore, unique properties of the ionic liquids designed and selected, which exhibit a high capability to absorb the organic solutes from the vapor phase above room temperature, together with their minimal volatility and thermal stability (in some case above 300 °C) opens up new opportunities to academia and industry. This process may be used to develop efficient and specifically designed equipment (for example, ionic liquids immobilized or incorporated in inorganic supports, such as particles and membranes) for the capture of valuable or environmentally toxic organic vapors directly from gaseous sources at high temperatures.

Experimental Section

General remarks: Chemicals 1,4-benzodioxane, xanthene, biphenyl, anthracene, and menthol were purchased from Aldrich and used as supplied. The synthesis and physical properties of ionic liquids used for the absorption study will be reported elsewhere. Each ionic liquid sample used for the absorption experiments was further purified by flash column chromatography (eluent: dichloromethane) followed by removal of the volatile components under high vacuum (5×10^5 mbar) at room temperature for 5 h. Flash chromatography was carried out on silica gel 60 M from MN (ref. 815381) or on aluminium oxide basic from MN (ref. 815010, Brockmann activity 1).

NMR spectroscopy: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX400 Spectrometer. Chemical shifts are reported downfield in parts per million (ppm) from a TMS reference.

IR spectroscopy: IR spectra were recorded on a Jasco FTIR spectrometer as thinly dispersed films.

Gas Chromatography: The quantity of 1,4-benzodioxane, biphenyl, xanthene, and menthol absorbed onto the ionic liquids was measured by using model Finnigan Focus GC from the Thermo Electron Corporation (USA). A standard addition method was used for the accuracy of the results. GLC analysis: column Restek; ref. RTX-5; (5 m × 0.32 mm); carrier gas flow: 0.9 mL min^{-1}; T(oven) = 160, T(injector) = 270, T(detector) = 250 °C.

Water absorption measurement: The water content of each ionic liquid was determined by a volumetric Aquastar Karl Fischer titration. Samples of all compounds were dissolved in dichloromethane and titrated with a step of 250 µL.

General procedure for the absorption experiments carried out by using ionic liquids: A specially devised glass chamber of capacity 200 mL was used for the absorption study. The organic solute (2 g) was placed at the bottom of the flask over which iron mesh was kept. The ionic liquid to be tested was put into the special vials of diameter 1 cm and capacity 1 mL with a small magnetic stirrer. These vials containing ionic liquids were laid on the top of the iron mesh. Air of 15 cm^3 min^{-1} was blown inside the assembly. The whole equipment was kept in an oil bath at a constant temperature of 50 °C. The gas generated slowly got absorbed into the ionic liquid. Absorption runs were performed for 48 h.

Further, the ionic liquid which contained organic solute was passed through a column of silica for desorption and analysis. A mixture of 40 % ethyl acetate in ether was used as the eluent. The eluent free from ionic liquid contained the organic solute, which was absorbed onto the ionic liquid. The percentage absorption of organic solute on the ionic liquids (µg of solute per g of IL) was determined by using the gas chromatography method (GLC). Benzophenone was added to each final sample as an internal standard. The percentage of 1,4-benzodioxane ($t_R = 0.77$ min), biphenyl ($t_R = 1.18$ min), xanthene ($t_R = 2.73$ min), and menthol ($t_R = 0.74$ min) was determined by a comparison with the peak area of the benzophenone ($t_R = 2.51$ min). In Figures 6–8, examples of GLC chromatograms obtained for absorption from an air stream containing a mixture of 1,4-benzodioxane and biphenyl in different ionic liquids are provided.

General procedure for the analysis of organic solute in the vapor phase: The concentration of organic solute in the vapor phase was analyzed by performing an ionic liquid blank experiment at 50 °C. A 100 mL syringe was used for the collection of vapors from the glass chamber and was then dissolved into the eluent which contained the internal standard (benzophenone). The results were obtained by using the prior calibration measurements.

General procedure for the absorption of water vapors: The experiments for water-vapor absorption by ionic liquids were carried out at 50 °C for 48 h. The difference in water content values between final (after absorption) and initial (before absorption) gave the exact value of absorption for each ionic liquid. The initial water content was measured after leaving the ionic liquids for 24 h under vacuum (< 1 mbar).

General procedure for the desorption experiments: After the absorption experiments, the vials containing the ionic liquid and organic solute were put into the vacuum apparatus system, which consisted of a glass chamber in which the vials were introduced. The glass chamber was connected to a trap at low temperature (by using liquid nitrogen). The apparatus was kept in the oil bath at a constant temperature of 50 °C under vacuum (0.1 mbar) for 12 h. The trap was washed with dichloromethane and the percentage absorption of organic solute in the ionic liquids (µg of solute per g of ionic liquid) was determined by using gas chromatography (GLC) and internal standard method. The same ionic liquid can be further reused for the absorption process.

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