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Standard and Absolute pK_a Scales of Substituted Benzoic Acids in Room Temperature Ionic Liquids

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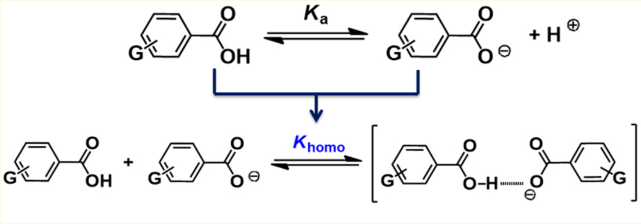
Ⓢ *Supporting Information*



ABSTRACT: Equilibrium acidity (pK_a) scales of 15 substituted benzoic acids in four room temperature ionic liquids (RTILs), BmimOTf, BmimNTf$_2$, BmpyNTf$_2$, and Bm$_2$imNTf$_2$, were established under standard conditions using a modified indicator overlapping method. The effect of homo hydrogen bonding on equilibrium acidity was calibrated, and the derived pK_a values were evidenced to be free from ion-paring complication. Regression analyses demonstrated that all of the pK_a scales obtained in four RTILs are linearly correlated to each other with an *R* value better than 0.996. These scales are also correlated well with the pK_a values in DMSO and with the corresponding gas-phase acidities with regression coefficients of 0.993 and 0.992, respectively. In addition, both the cation and anion of the ionic liquids were found to play a role in affecting the acidity of carboxylic acid.

■ INTRODUCTION

Equilibrium acidity[1] (i.e., pK_a) is the most frequently used physicochemical parameter, has played important roles in developing modern theories of organic chemistry, and has found very broad applications in related fields.[2−5] Over the past half of a century, several well-known pK_a scales of organic compounds in many conventional molecular solvents, including those in water, DMSO, acetonitrile (AN), THF, and others were established.[6−9] However, attention has been only recently brought to pK_a values in room temperature ionic liquids,[10] the emerging solvent system that has aroused a booming research enthusiasm over the past decade because of its very interesting and frequently quite different chemistry compared to that in molecular solvents,[11] which have rarely been investigated.[12]

To understand the chemistry in RTILs, there have been several exploratory studies over the past decade on acid/base behaviors in ionic liquids. For example, Gilbert and co-workers studied the Hammett function, H_0, of Brønsted acids HOTf and HNTf$_2$ in acidic ionic medium.[13] Turmine et al. reported the dissociation constants of a few acid−base pairs in a water−BmimBF$_4$ mixture.[14] D'Anna and Noto performed several series of measurements in ionic liquids on equilibrium constants of aliphatic amines and carboxylic acids with *p*-nitrophenol and *p*-nitrophenolate as indicators, respectively.[15,16] More recently, Siani et al. measured the equilibrium constants of ion-pair formation for some pyridines with trifluoroacedic acid and found that the basicity order is the same in ionic liquid as it is in water.[17] Most recently, Kumar et al. also studied the strength of carboxylic acids in RTILs using the Hammett function, H_0.[18] One may have noted that in these works the measured acidity or basicity in ionic liquid was actually referenced to the pK_a of the indicator in water. Therefore, the reported data should be regarded as relative values that do not directly reflect bond heterolysis free energies in ionic liquid. Moreover, because some molecular additives (such as water, dioxane, methanol, Brønsted acid, etc.) were unavoidably used in these measurements (i.e., mixed molecular ionic solvents had to be applied for practical purposes), the experimental conditions cannot be considered as standard. Additionally, the coverage of pK_a values was limited to no greater than 2 to 3 p*K* units for each substituted acid or base family because of the use of a single indicator acid as the reference. Very recently, it is encouraging to note that Doherty et al. determined the absolute pK_b of N-centered bases in ionic liquid by an electrochemical method. However, the uncertainty of the measurement is fairly large (±0.4−1.0 p*K* units), and the substrates suitable for this method have to be limited to amines only.[19]

Not long ago, we developed a method to measure precisely the absolute pK_a values (SD $\leq \pm$ 0.05 p*K*) in pure ionic liquids[21] based on our years of expertise in determining absolute pK_a values in DMSO and in their related applications.[22] In that work, the standard ionic solvent systems and standard experimental conditions for absolute acidity measurement were outlined.[21] The pK_a values of a series of carbon acids that are suitable to serve as acid−base equilibrium indicators for pK_a measurement in IL were determined over an acidity range as broad as 13 p*K* units (Scheme 1). This initial pK_a scale of the indicators should be applicable to measure the

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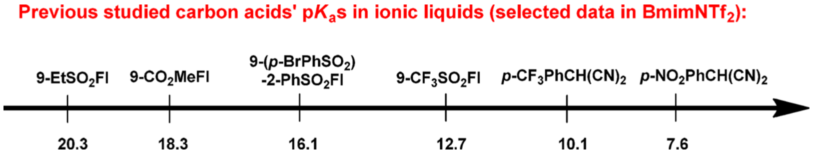
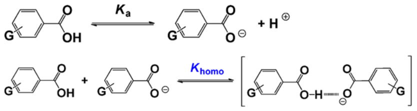
Scheme 1. pK_a Values of the Indicator Carbon Acids[20] (SD ≤ ±0.1) Measured in Our Previous Work[21]



pK_a values of many compounds of interest. In the present work, we extended our continued effort in understanding bond energetics in solution to the acidities of oxygen acids (i.e., 15 substituted benzoic acids) in RTILs. The reason for choosing this family of substrates as the target is because of their general importance in both physical organic studies[4] and their synthetic applications.

It should be pointed out that because of the significant difference between the O−H acids of this work and the C−H acids studied earlier in the effect of hydrogen bonding care must be taken when evaluating the pK_a data for benzoic acids. As indicated in the literature,[23,24] intermolecular hydrogen-bonding interactions, also known as homo conjugation, as shown in equilibrium 2, may complicate the acidity measurement of oxygen acids, and this effect needs to be calibrated because it could be quite substantial (more on this later). Previous attempts to evaluate the acidities of carboxylic acids in a MeOH-IL system[16] may bear unknown uncertainty because of neglecting the homoconjugation effect.

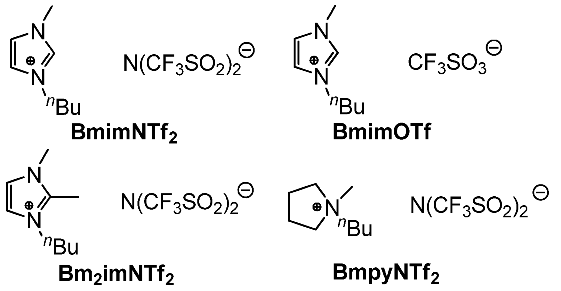


equilibrium 1

equilibrium 2

In the present work, the complication brought in by H-bonding interactions to the true equilibrium acidity has been calibrated with a strategy similar to that of Bordwell for evaluating the acidities of oxygen acids in DMSO.[24] Both the pK_a values and homoconjugation constants (K_{homo} in equilibrium 2) of benzoic acids were measured. As a result, the absolute pK_a scales of benzoic acids in four pure RTILs (Scheme 2) were established. Medium effects on acidities and homoconjugation were discussed.

Scheme 2. Structures of Ionic Liquids Used in This Work



■ RESULTS AND DISCUSSION

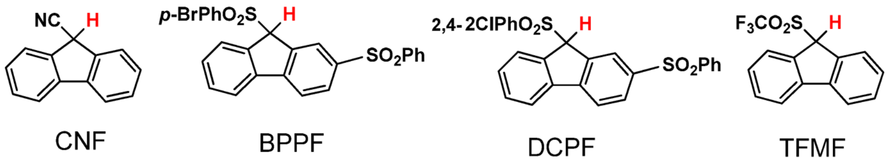
General Strategy. On the basis of our earlier study,[21] four standard RTILs, BmimNTf$_2$, BmpyNTf$_2$, Bm$_2$imNTf$_2$, and BmimOTf (Bmim$^+$ = 1-butyl-3-methylimidazolium, Bmpy$^+$ = *N*-butyl-*N*-methylpyrrolidinium, and Bm$_2$im$^+$ = 1-butyl-2,3-dimethylimidazolium) were used as the media (Scheme 2), and four carbon acids with known pK_a (Scheme 3) were rationally selected as indicators in the present work. It should be kept in mind that in a pK_a measurement the acidity of the indicators selected or of the unknown acids under investigation should be no less than 2 to 3 pK units stronger than that of the solvent to avoid a contribution of the solvent proton to acid/base equilibria 1 and 2. This requirement is obviously met in the present study because the equilibrium acidity of the least acidic indicator used here (9-cyanofluorene, pK_a 8.3 in DMSO[7b]) is tremendously stronger than that of the imidazolium salt BmimOTf (pK_a 22.0 in DMSO[22d]).

The pK_a values and the K_{homo} hydrogen-bonding constants in ionic liquids were determined through acid−base titration (see the Experimental Section).[21] The respective pK_a and K_{homo} values were obtained with a complex multivariate regression equation derived from equilibria a and b shown in Scheme 4.[24] The standard deviations for various benzoic acids were typically within ±0.1 pK units, and the agreement between different runs using different indicators was excellent. The derived pK_a and K_{homo} values of benzoic acids in four RTILs together with the data of phenylacedic acid and 1-adamantane carboxylic acid (ACA) in BmimNTf$_2$ are presented in Table 1.

Effect of Anion and Cation Moieties on Acidity. As shown in Table 1, the pK_a values of the selected benzoic acids cover a range of 12.0−13.6, 13.05−15.7, 14.1−16.9, and 14.2−17.1 in BmimOTf, BmimNTf$_2$, BmpyNTf$_2$, and Bm$_2$imNTf$_2$, respectively. The observed acidity changes of benzoic acids in different RTILs indicate that the acidifying ability of ionic liquid varies when altering the composition and structure of the IL. Comparison of the acidity values of benzoic acid in these RTILs (13.3, 15.15, 16.3, and 16.5) with its corresponding pK_a values in DMSO (11.0) and water (4.2) immediately reveals that the solvation stabilizing effect of these commonly used ionic media toward proton is, in fact, considerably weaker than that of the highly polar protic (like water) or aprotic (like DMSO) molecular solvent. Further inspection of the data in ILs reveals that the pK_a values in BmimOTf are about 2−4 pK units lower (i.e., more acidic) than those in the other three ILs with NTf$_2^-$ as a common anion, which is similar to the phenomenon observed previously for C−H acids.[21] Again, this should be ascribed to a more localized negative charge and smaller size of OTf$^-$ compared to NTf$_2^-$, both leading to a stronger solvation effect on proton.

The data further show that varying the structure of the cation of ionic liquid also has a quite notable influence on acidity, although it is not as strong as the effect of its counteranion. As seen, the general trend of the pK_a order brought in by different cations are Bm$_2$imNTf$_2$ > in BmpyNTf$_2$ > in BmimNTf$_2$ for all benzoic acids, which may be rationalized by considering the difference of the cation of ionic liquid in charge delocalization and in the accessibility of its positive charge toward benzoate anion (or toward the strongest nucleophile in a system, as addressed in the recent literature[25]). As seen from Scheme 2, the Bmim$^+$ cation bears three protons with hydrogen-bonding potential at the C2, C4, and C5 positions of the ring, and it is also the least hindered cation among the three cations under comparison; hence, the pK_a values in BmimNTf$_2$ are indeed

Scheme 3. Indicators Used in This Work and Their pK_a Values in RTILs (standard deviations: ≤ ±0.1) [21]



	CNF	BPPF	DCPF	TFMF
$BmimNTf_2$[a]	16.7	16.1	15.0[26]	12.7
$BmpyNTf_2$[a]	16.6	16.0	15.0_5[26]	12.6
Bm_2imNTf_2[a]	17.4	16.5	–	13.2
BmimOTf[a]	13.8	13.3	12.4[26]	10.0

Scheme 4. Typical (a) Acid-Base Equilibrium and (b) Homoconjugation Involved in pK_a Evaluation

$$HA + In^- \xrightleftharpoons{K_{eq}} HIn + A^- \qquad HA + A^- \xrightleftharpoons{K_{homo}} HA\text{----}A^-$$

$$K_{HA} = \frac{[HIn]\,[A^-]}{[In^-]\,[HA]} \qquad K_{homo} = \frac{[HA\text{----}A^-]}{[A^-]\,[HA]}$$

(a) (b)

observed to be the lowest. However, the slightly higher pK_a value in Bm_2imNTf_2 than in $BmpyNTf_2$ may be understood by a greater delocalization of the positive charge in Bm_2im^+ than in $Bmpy^+$, making Bm_2im^+ less accessible to benzoate ions than the latter. Thus, it is clear that both the cation and anion of IL, but not the anion only as reported in the literature,[12−16] can affect acidic dissociation of benzoic acids in ionic media. Actually, the effect of cation of ionic liquid on tuning the pK_a is observed to be even greater here for benzoic acid than for the C−H acids studied before[21] (average pK_a variation is ~1.3 vs ~0.7 pK units for O−H and C−H acids, respectively), which can be ascribed to its closer and thus stronger solvation of the cation with oxanion than with carbanion. This is because, compared to carbanion, the more localized negative charge on benzoate ion and its smaller size allow this oxanion to get closer to the cation of the ionic liquid, so it becomes more sensitive to the changes in the charge and structure of its counterpart.

Regression Analysis. To examine the electronic effect in ionic solvent, regression analysis was carried out. Excellent linear Hammett plots (R = 0.997−0.998) were observed for para-substituted benzoic acids (Figure 1), revealing that there should be no fundamental difference for a remote substituent to influence electronically the bond acidic dissociation in molecular solvent and in ionic media. Although this should not be a surprise, it was not observed in other RTILs in previous acidity/basicity studies except in our work. Further inspection of Figure 1 reveals an interesting trend in the slope of the lines, which changes as the composition and structure of the ionic liquid is altered, and in the absolute value of the slope,

Table 1. pK_a Values and Homo-Hydrogen-Bonding Constants (K_{homo}) of Benzoic Acids, Phenylacetic Acid, and 1-Adamantane Carboxylic Acid in ILs

		$BmimNTf_2$		$BmpyNTf_2$		Bm_2imNTf_2		BmimOTf	
substituents	σ	pK_a[a]	log K_{homo}[a]	pK_a[a]	log K_{homo}[a]	pK_a[a]	log K_{homo}[a]	pK_a[a]	log K_{homo}[a]
p-MeO	−0.27	15.7[b]	3.7[b]	16.9[e]	4.2[e]	17.1[d]	4.1[d]	13.6[d]	2.4[d]
p-$C(CH_3)_3$	−0.20	15.5[b]	3.4[b]	16.6[d]	4.0[d]	16.9[d]	4.0[d]	13.5[d]	2.5[d]
p-CH_3	−0.17	15.3_5[b]	3.6[b]	16.5[d]	4.0[d]	16.7_5[d]	3.9[d]	13.5[d]	2.6[d]
p-C_6H_5	−0.01	15.0[b]	3.5[b]	16.2[d]	3.9[d]	16.3[d]	3.9_5[d]	13.2[d]	2.6[d]
H	0.00	15.1_5[b]	3.5_5[b]	16.3[d]	4.0_5[d]	16.5[d]	4.0[d]	13.3[d]	2.7[d]
p-F	0.06	14.9[b]	3.5[b]	16.0[d]	4.0[d]	16.2_5[d]	3.9_5[d]	13.0[d]	2.9[d]
p-Br	0.23	14.5[b]	3.5[b]	15.6[d]	4.0[d]	15.8[d]	3.9_5[d]	12.8[d]	2.9[d]
p-Cl	0.23	14.4[b]	3.4[b]	15.5[d]	4.0[d]	15.7[d]	4.0[d]	12.7_5[d]	3.0[d]
p-CF_3	0.54	13.6[c]	3.4[c]	14.6[b]	3.8_5[b]	14.7[c]	3.5[c]	12.4[b]	2.7[b]
p-CN	0.66	13.3[c]	3.3[c]	14.4[b]	3.8[b]	14.5[c]	3.5[c]	12.2[b]	2.7[b]
p-NO_2	0.78	13.0_5[c]	2.7[c]	14.1[c]	3.3[c]	14.2[c]	3.5_5[c]	12.0[b]	2.9[b]
m-MeO	0.12	14.7[b]	3.2[b]	15.9[d]	3.9_5[d]	16.4[d]	3.9[d]	13.1[d]	2.8[d]
m-Cl	0.37	14.1_5[b]	3.2[b]	15.3[b]	3.8[b]	15.5[d]	3.9[d]	12.6[b]	2.6[b]
m-NO_2	0.71	13.1[c]	3.0[c]	14.1_5[c]	3.2[c]	14.3[c]	3.5_5[c]	11.9[b]	2.8[b]
m-Me	−0.07	15.2_5[b]	3.5_5[b]	16.4[d]	4.0_5[d]	16.7[b]	4.0[b]	13.4[d]	2.7[d]
$PhCH_2COOH$		15.6[e]	3.5[e]						
ACA		17.0[b]	3.6[b]						

[a] In pK and log K units; SD ≤ ±0.1. [b] Measured with indicator DCPF, 9-(2,4-dichlorophenylsulfonyl)-2-(phenylsulfonyl)fluorene.[26] [c] Measured with indicator TFMF, 9-trifluoro-methylsulfonylfluorene.[21] [d] Measured with indicator BPPF, 9-(p-bromophenylsulfonyl)-2-(phenylsulfonyl)-fluorene.[21] [e] Measured with indicator CNF, 9-cyanofluorene.[21]

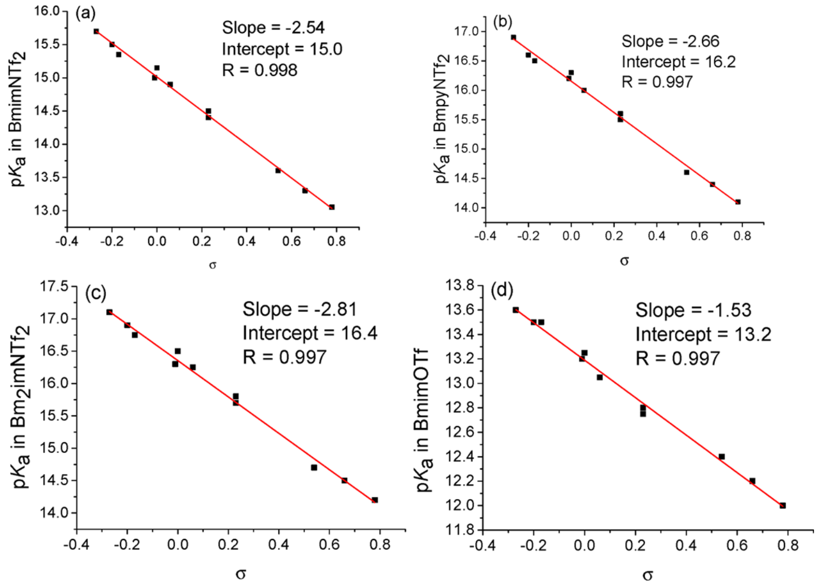


Figure 1. Hammett plots for pK_a values of benzoic acids (SD ≤ ±0.1 pK) in (a) $BmimNTf_2$, (b) $BmpyNTf_2$, (c) Bm_2imNTf_2, and (d) BmimOTf.

Table 2. Acidity Data in $BmimNTf_2$, H_2O,[28] and DMSO[6c] as Well as in the Gas Phase[29]

substituents	pK_a ($BmimNTf_2$)[a]	pK_a (ΔG) (gas phase)[b]	pK_a (H_2O)[c]	pK_a (DMSO)[d]
p-CH_3	15.3_5	244.7 (333.8)	4.3_5	11.2
H	15.1_5	244.1 (333.0)	4.2	11.0
p-F	14.9	241.9 (330.0)	4.1_5	
p-Br	14.5		4.0	10.2
p-Cl	14.4	240.8 (328.5)	4.0	10.1
p-CN	13.3		3.5_5	9.2_5
p-NO_2	13.0_5	235.4 (321.1)	3.4_5	9.1

[a] In pK units; SD ≤ ±0.1. [b] Converted to pK units from the literature values of ΔG (in parentheses) in kilocalories per mole, SD ≤ ±1.5. [c] In pK units; SD ≤ ±0.2. [d] In pK units; SD ≤ ±0.2.

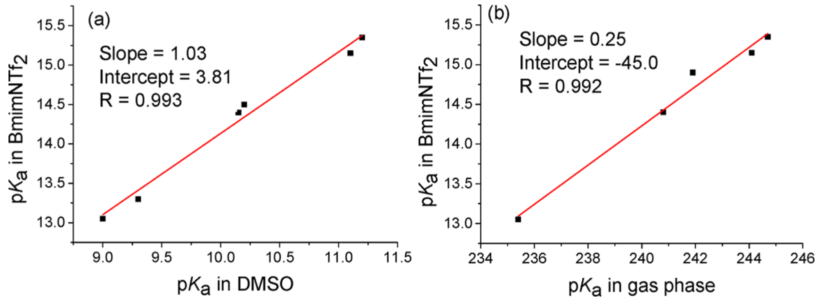


Figure 2. Correlation analyses for the acidities of benzoic acids in IL, molecular solvent, and the gas phase: (a) pK_a values in $BmimNTf_2$ vs pK_a values in DMSO (SD ≤ ±0.1 pK) and (b) pK_a values in $BmimNTf_2$ vs pK_a values in gas phase (SD ≤ ±1.5 pK).

which varies with different RTILs in the order BmimOTf (−1.53) < $BmimNTf_2$ (−2.54) < $BmpyNTf_2$ (−2.66) < Bm_2imNTf_2 (−2.81). This trend is seemingly related to the strength of the respective ionic liquid to stabilize the proton and benzoate ion after acidic dissociation because, as mentioned above, the acidities of benzoic acid in different ILs were also found to follow the same order: BmimOTf (13.3) < in $BmimNTf_2$ (15.15) < in $BmpyNTf_2$ (16.3) < in Bm_2imNTf_2 (16.5).

One other phenomenon worth noting is that the pK_a values of p-Ph-PhCOOH ($\sigma = -0.01$) in all four ILs used are 0.1 to 0.2 pK units lower than the parent benzoic acid. We speculate that the cation−π and anion−π interaction between the ILs and the aromatic ring of the p-Ph substituent may be responsible for this somewhat anomalous observation.[27]

In addition, excellent straight lines with R values of 0.997−0.999 were obtained in regression analysis among the pK_a scales of benzoic acids in the four RTILs (Figure S6). Again, the slope changes in a similar order, Bm_2imNTf_2 (1.12) > $BmpyNTf_2$ (1.05) > BmimOTf (0.6), which corresponds nicely with the trend of the changing slopes observed in different ionic liquids.

Table 2 shows the acidity data of benzoic acids in $BmimNTf_2$ (this work), H_2O,[28] and DMSO[6c] as well as in the gas phase.[29] The most obvious feature of the table is the substantial drop of the absolute acidity values in these solvents as compared to those in the gas phase, reflecting the dramatic power of solvation in strengthening acidity, with an acidifying order of water > DMSO > IL. Interestingly, one may also note that the span of the data as the substituent changes from *p*-Me to *p*-NO_2 is 0.9, 2.1, 2.3, and 9.3 (12.7 kcal) p*K* units in water, DMSO, IL, and the gas phase, respectively, indicating the sensitivity of the substituent effect in the respective media. The Hammett ρ values in the corresponding solvents and gas phase provide a more obvious comparison of the substituent effect with a similar trend, that is, in water (−1) < in DMSO (−2.32) < in IL (−2.54) < in gas phase (−10.0) (cf. Figure S7). This order, again, corresponds well with their order of the acid-strengthening solvation effect of the ionic liquids mentioned above. Comparison of the acidities of benzoic acids in ionic liquid with their counterparts in molecular solvents and in the gas phase may also give important information on the nature and the quality of the measured data. To our delight, good linear correspondence was also observed (Figure 2) when the IL phase acidity is plotted against those in DMSO and in the gas phase, with $R = 0.993$ and 0.992, respectively. The very good linearity of the correlations indicates that the acidity scales obtained in these RTILs are intrinsic in nature.

Homo Hydrogen Bonding. During the pK_a measurement of the parent benzoic acid, a standard overlapping indicator method was employed, which was applied successfully in our previous work on the pK_a measurement of carbon acids in ILs. However, in the current work, we observed that the initially evaluated pK_a values of benzoic acid gradually decreased after consecutively adding benzoic acid solution into the solution containing the indicator base. The value resulting from the first titration (a drop) is 0.8 p*K* higher than the one from the last titration in a 10 aliquot titration. Because this is the typical phenomenon of homoconjugation, which was also seen in Bordwell's measurement of benzoic acids in DMSO (equilibrium 2),[24] the intermolecular H-bonding effect (Table 1, K_{homo}) in the present case was hence evaluated through a modified model (based on equilibrium 3, taking $BmimNTf_2$ as example) that differs from the one used previously for carbon acids.

$$PhCOO^{-}\text{----}Bmim^{+} + PhCOOH\text{----}NTf_2^{-} \xrightleftharpoons{K_{homo}} Bmim^{+} + NTf_2^{-} + PhCOOH\text{----}{}^{-}OOCPh \qquad \text{equilibrium 3}$$

From the homo-hydrogen-bonding constants (K_{homo}) presented in Table 1, it is clear that these interactions are fairly strong and different in extent for the O−H acids in these four ILs. Interestingly, the change of K_{homo} for these O−H acids is approximately in the order of $Bm_2imNTf_2 \approx BmpyNTf_2 > BmimNTf_2 > BmimOTf$, which is the opposite of the order of the solvent effect in the respective ionic liquids. This should not be difficult to conceive, however, by considering that a stronger solvation would lead to stronger binding of solvent with substrate compared to the homo hydrogen bonding between substrate molecules.

■ CONCLUSIONS

Absolute equilibrium acidity scales of 15 benzoic acids in four pure RTILs were established. The pK_a platform of the indicators developed earlier by our group is confirmed to be applicable for precisely measuring standard pK_a values of oxygen acids in RTILs as well. A modified indicator overlapping method was introduced to the present acidity study to overcome the complication caused by the homo-hydrogen-bonding interaction between the parent O−H acid and the corresponding oxanion. Regression analyses among the pK_a values in various ionic liquids and between the data derived from different phases (ionic, molecular, and the gas phase) are all linear, confirming the intrinsic nature and high quality of the measured data. Moreover, comparisons of the acidity values in ILs carrying different anion or cation directly indicate that the pK_a variation of the same acid in different ionic liquid is brought in by the varying ability of the acid-strengthening effect of the ionic liquid.

■ EXPERIMENTAL SECTION

Materials. Ionic liquids were synthesized and purified on the basis of literature procedures.[30] The indicators used were synthesized and characterized by known methods.[8a] All of the benzoic acids were commercially available. Solid substrates and other commercial reagents used for synthesis were carefully recrystallized and dried before use. The solutions of indicators, acids, and base were prepared by the procedure in a previous work.[21]

Details of Measurement. All manipulations were carried out under dry argon using standard Schlenk techniques.

Equipment. The indicator and acid reservoirs, p*K* cell, and syringes for pK_a measurement in ionic liquids were the same as described before.[21] All weights were recorded to ±0.0001 g, and the absorbance was measured with a UV/vis spectrophotometer.

pK_a and K_{homo} Measurement in Ionic Liquids. The procedure of pK_a and K_{homo} measurement of benzoic acid in ionic liquid was similar to that for the measurement of C−H acids.[21] In a typical run, a particular ionic liquid and a small amount of base were added into a p*K* cell of known weight, the cell was weighed again, and a baseline was recorded on a UV/vis instrument. Upon adding the solution of an indicator of known pK_a, both the spectrum and the weight for each addition (6−8 additions in total) were recorded. After an excess amount of indicator solution was added and the absorption was recorded (from which the absorption coefficient was evaluated), the target acid of unknown pK_a was added in several aliquots (8−10 consecutive titrations). The weight of the cell and the corresponding spectrum were recorded upon each addition. With the data derived from the change of absorbance, the corresponding pK_a and K_{homo} were evaluated with a complex multivariate regression equation aforementioned.[24] The pK_a values in Table 1 are averages based on at least three to five such runs and were found to be reproducible within ±0.1 pK_a unit.

Investigation of Ion-Pairing Effect. Cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane), an excellent K^+ scavenger, was added to the system under acidity measurement to examine whether there exists ion pairing between K^+ and benzoate anion, which should be avoided for the measurement of a standard pK_a. It was shown that there was no notable change between the results obtained in the presence and in the absence of cryptand 222, indicating that perturbations of the ion-pairing effect on acidity of benzoic acid in ionic liquid were minimized under the experimental conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Structure of C−H acids listed in Scheme 1; pK_a values of PhCOOH in $BmimNTf_2$ measured with CPPF using the unmodified indicator overlapping method upon adding respective droplets of acid; pK_a and log K_{homo} values of PhCOOH in $BmimNTf_2$ measured by modified indicator overlapping method in different runs; absorption spectra of the anion derived from DCPF for various added amount of DCPF or *p*-$C(CH_3)_3$-PhCOOH during the titration in $BmimNTf_2$; absorption spectra of the anion derived from DCPF for various added amount of DCPF or (b) PhCOOH during the titration in $BmimNTf_2$; absorption spectra of the anion derived from TFMF for various added amount of TFMF or (b) *p*-NO_2-PhCOOH during the titration in $BmimNTf_2$; absorption spectra of the anion derived from TFMF for various added amount of TFMF or *m*-NO_2-PhCOOH during the titration in $BmimNTf_2$; absorption spectra of the anion derived from CNF for various added amount of CNF or ACA during the titration in $BmimNTf_2$; linear regression between pK_a values of benzoic acids in $BmimNTf_2$, $BmpyNTf_2$, Bm_2imNTf_2, and BmimOTf; and Hammett plots for the pK_a values of benzoic acids in DMSOand in the gas phase. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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