

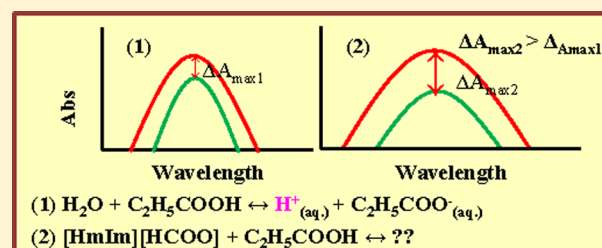
Probing the Acidity of Carboxylic Acids in Protic Ionic Liquids, Water, and Their Binary Mixtures: Activation Energy of Proton Transfer

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Supporting Information

ABSTRACT: Acidity functions were used to express the ability of a solvent/solution to donate/accept a proton to a solute. The present work accounts for the acidity determination of HCOOH, CH₃COOH, and CH₃CH₂COOH in the alkylimidazolium-based protic ionic liquids (PILs), incorporated with carboxylate anion, water, and in a binary mixture of PIL and water using the Hammett acidity function, H_0 . A reversal in the acidity trend was observed, when organic acids were transferred from water to PIL. It was emphasized that an increased stabilization offered by PIL cation toward the more basic conjugate anion of organic acid was responsible for this anomalous change in acidity order in PILs, which was absent in water. The greater stabilization of a basic organic anion by PIL cation is discussed in terms of the stable hard–soft acid base (HSAB) pairing. A change in the H_0 values of these acids was observed with a change in temperature, and a linear correlation between the $\ln H_0$ and $1/T$ was noted. This relationship points toward the activation energy of proton transfer (E_{a,H^+}), a barrier provided by the medium during the proton transfer from Brønsted acid to indicator. The H_0 function in binary mixtures points to the involvement of pseudosolvent, the behavior of which changes with the nature and concentration of acid. The presence of the maxima/minima in the H_0 function is discussed in terms of the synergetic behavior of the pseudosolvent composed of the mixtures of aqueous PILs.



INTRODUCTION

For the past few years, there has been a stupendous increase in the search of alternatives to volatile organic compounds (VOCs) due to environment pollution. Ionic liquids (ILs) are considered as a substitute to these VOCs. The initial interests in ILs emerged because of their negligible vapor pressure, low melting point, high thermal stability, wide electrochemical window, inflammability, recyclability, and so on.^{1,2} ILs have been divided into two major classes depending on the quaternization process, i.e., either by an alkyl group (–R) or a proton (H⁺). Quaternization by an alkyl group results in an aprotic ionic liquid (AIL), while quaternization by H⁺ results in a protic ionic liquid (PIL). Similar to PILs are Brønsted acidic ionic liquids, in which protons occupy either the cation or the anion (not necessarily on the cation as in PILs), and therefore, they are classified as PIL/AILs, respectively. Unlike AILs, PILs contain dissociable protons in their continuum medium that makes them a suitable nonaqueous electrolyte for polymer membrane fuel cells.³ The alkylammonium-based PILs have been observed equally applicable for catalytic media, biological applications, explosive formulations, and lubricants.⁴ Ethylammonium nitrate (EAN) is extensively used in biological applications as solvent media because it offers stabilization to proteins through various specific and nonspecific interactions.^{5,6} PILs were extensively used in chromatography because of their highly polar nature, ease in availability, stability toward air/water, and selective interactions with solute.⁷

PILs were often categorized as “poor ionic liquids” based upon the Walden plot.⁸ Unlike, AILs, where ionic species predominate, PILs contain neutral species along with the ionic moieties, which materialize either due to the aggregation of ions or the retro-transfer of a proton from the cation to the anion.⁹ The fraction of ionic species present in a medium can be referred to in terms of the “ionicity concept”. Various techniques such as NMR, Walden’s fluidity–conductivity plot, $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$, and IR spectroscopy are used in the qualitative evaluation of the ionicity of ILs.¹⁰ Angell et al. pointed out that the ΔpK_a ($pK_a(\text{acid}) - pK_a(\text{base})$) could be a useful parameter to direct the degree of proton transfer between the Brønsted acid and Brønsted base, and a nearly ideal Walden behavior was observed for $\Delta pK_a > 8$.¹¹ However, these neutral moieties when present in a very small amount were considered as a continuum of PIL.¹² The presence of the extensive hydrogen bonding stabilizes both the cation and anion in PILs, therefore reducing the formation of the neutral moieties due to the retro-transfer of proton.¹³ PILs were usually preferred as media to carry out many acid-catalyzed reactions due to the presence of an acidic proton.¹⁴ However, their use in various processes such as pharmacological application, reaction mechanism, properties of new materials, changing molecular structure, etc., requires precise information about the acidity level. Several attempts

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have been made to estimate the acidity of PILs using different acidity scales.¹⁵ Though PILs contain an acidic proton, their acidity can further be tuned by mixing with a Brønsted acid.

The most interesting properties of ILs are governed by the various specific and nonspecific interactions between ions.¹⁶ Hydrogen bonding plays an important role in strengthening the interactions between the constituent ions and therefore influencing the properties such as viscosity and melting point of these Coulomb systems.¹⁷ A PIL resembles water in the sense of extensive hydrogen bonding that makes them a hyperpolar medium.¹⁸ The hyperpolar behavior is equally supported by a high relative permittivity (ϵ), close to water, and high $E_T(30)$ value for alkyl ammonium-based PILs.¹⁹ However, according to a recent development on the polarity of alkyylimidazolium-based PILs, the hyperpolarity is limited only to the oxyanions such as NO_3^- , HSO_4^- , PO_4^{3-} , etc. On the other hand, more basic organic anions such as HCOO^- , CH_3COO^- , and $\text{CH}_3\text{CH}_2\text{COO}^-$ lead to lower polarity.²⁰

In spite of being a subject of extensive investigation in various applications from very early development of PILs, a little research has been carried out on the acidity formulation of these nonaqueous media. The acid–base notion for a variety of compounds was based on their $\text{p}K_a$ values. Since $\text{p}K_a$ is more useful only for aqueous medium, alternate methods such as potentiometric titration and acidity functions have been used for nonaqueous media. By using potentiometric titration and acidity functions, the pH value, which ranges from $1 < \text{pH} < 13$, can be extended on either end in aqueous/nonaqueous solvents.²¹ Unlike pH, which indicates the total strength of protons, an unconventional method like the Hammett function observes the variation of any physical property due to the protonation. Acidity determination of weak acids and bases in nonaqueous medium by a spectroscopic method depends on the isolation of spectral changes due to the protonated/non-protonated forms of the indicator. For most of the indicators, the isosbestic point was observed, which points out the appearance of protonated/non-protonated forms.²² A large number of acidity functions depending on the acidity and basicity of the medium are available in the literature. The determination of acidity function based on the primary nitroaniline as a base is well established because of the high accuracy in its measurement.

The first report on acidity determination in ILs came very recently when Thomazeau, Olivier-Bourbigou, Magna, Luts, and Gilbert measured the acidity of bistriflylimide acid (HNTf_2) and triflic acid (HOTf) in the imidazolium-based AILs.²³ They observed the same acidity level for HNTf_2 and HOTf in $[\text{BMIM}][\text{NTf}_2]$ (1-butyl-3-methylimidazolium bistriflimide). However, HNTf_2 showed a higher acidity level in $[\text{BMIM}][\text{BF}_4]$ (1-butyl-3-methylimidazolium tetrafluoroborate) than that in $[\text{BMIM}][\text{NTf}_2]$ because of the lesser solvation of proton (H^+) by BF_4^- than that of NTf_2^- . The role of C2–H (most acidic proton on the ring) on the acidity of HNTf_2 was negligible, as similar H_0 values were noted in $[\text{BMIM}][\text{BF}_4]$ and $[\text{BMMIM}][\text{BF}_4]$ (1-butyl-2,3-dimethylimidazolium tetrafluoroborate). Recently, a general account on the acidity of different carboxylic acids in $[\text{bm}_2\text{im}][\text{NTf}_2]$ (1-butyl-2,3-dimethylimidazolium bistriflimide) and $[\text{bmpyr}][\text{NTf}_2]$ (*N*-butyl-*N*-methyl pyrrolidinium bistriflimide) using spectrophotometric titration in terms of protonation equilibrium (K) has been published by Noto and co-workers.²⁴

In recent years, we have been investigating several physicochemical and physical organic aspects of ILs.^{25,26} In

the current investigation, we now address the issue of the acidity determination of carboxylic acids in the imidazolium-based PILs using the Hammett equation. We also attempt to establish a correlation between the acidity of these acids with the structural component of ILs. Efforts have been made to quantify the transfer of the acidity function from aqueous acid solution to aqueous ionic liquid. We have attempted to solve these issues by measuring the acidity in PILs, probing the thermal effect on the acidity function and subsequently by calculating the acidity in the binary mixtures of water–PILs. The carboxylic acids were chosen in order of the relative basicity of their conjugate anion in the gas phase. The structures of PILs used in the study are shown in Figure 1. The acronyms for ILs used in the present study are summarized in Table 1.

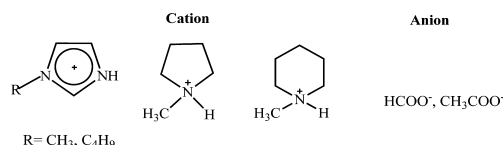


Figure 1. The structure of PILs used in the study.

Table 1. The Acronyms of PILs Employed in the Present Work

acronyms	names of ionic liquid
$[\text{HmIm}][\text{HCOO}]$	1-methylimidazolium formate
$[\text{HmIm}][\text{CH}_3\text{COO}]$	1-methylimidazolium acetate
$[\text{HbIm}][\text{HCOO}]$	1-butylimidazolium formate
$[\text{HbIm}][\text{CH}_3\text{COO}]$	1-butylimidazolium acetate
$[\text{HPyr}][\text{HCOO}]$	1-methylpyrrolidinium formate
$[\text{HPyr}][\text{HCOO}]$	1-methylpiperidinium formate

EXPERIMENTAL SECTION

Materials. A spectroscopic indicator dye 4-nitroaniline was obtained from Sigma Aldrich. 1-Methylimidazole, 1-butylimidazole, 1-methylpyrrolidine, and 1-methylpiperidine were purchased from Sigma and distilled prior to use. Formic acid, acetic acid, and propionic acid solutions were obtained from Merck and used as obtained. Deionized water possessing a specific conductance $< 0.055 \times 10^{-6} \text{ S cm}^{-1}$ was used throughout the work.

Synthesis of Protic Ionic Liquids. PILs were synthesized by a single-step atom economic reaction.^{18b} An equimolar amount of Brønsted acid was added dropwise into the Brønsted base placed under the ice bath followed by a vigorous stirring for 6 h at room temperature. Volatile impurities and water vapor escaped from the protic ionic liquids by placing it under a rotavapor. Remaining traces of water vapor were removed from the PIL by placing it under a high vacuum for 12 h. A colorless liquid was obtained and was kept inside the desiccator connected with a high vacuum. Before sampling, the water content in PILs as measured by the Karl Fischer coulometer was noted as less than 50 ppm. Since PILs were prepared from the halide free pathway, they were devoid of any halide impurities.

Measurement of Acidity Using the Hammett Equation. A dilute solution (10^{-4} M) of 4-nitroaniline dye (Figure 2) in methanol was prepared and used as a stock solution throughout the experiments. All the acids were used as an

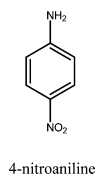


Figure 2. The acidity probe 4-nitroaniline.

equimolar solution in water.²⁷ Any contribution toward the maximum optical density by the medium was set to zero by using a baseline. A small amount of dye solution was dissolved in 1 mL of PIL, and methanol was removed by placing it under a high vacuum. The whole sample was now filled inside the quartz cuvette, and the UV–visible spectrum was recorded. The maximum optical density/absorbance (A_{\max}) for PIL + dye solution was used as a reference for each PIL. An addition of acid in PIL + dye content protonates the dye, therefore decreasing the maximum optical density. Similarly, A_{\max} after each addition of acid was recorded and again compared with the A_{\max} of PIL + dye solution (Figure S1, Supporting Information). This relative comparison between A_{\max} of PIL + dye solution and PIL + dye + acid solution gave the relative abundance of the protonated and non-protonated forms of the dye. The acidity of the solution can be calculated by using the Hammett equation in the form of H_0 , the acidity function as given:

$$H_0 = \text{p}K(I)_{\text{aq}} + \log[I]_{\text{s}}/[HI^+]_{\text{s}} \quad (1)$$

where $\text{p}K(I)_{\text{aq}}$ is the protonation constant of the dye in aqueous solution. For 4-nitroaniline, $\text{p}K(I)_{\text{aq}} = 0.99$ and $[I]_{\text{s}}$ and $[HI^+]_{\text{s}}$ are the concentrations of solvated non-protonated and protonated forms of the indicator. From eq 1, it is clear that strong acid leads to the lower H_0 values.

Equation 1 can also be written as

$$H_0 = -\log a(H_{\text{aq}}^+) - \log \gamma(I)/\gamma(HI^+) - \log \Gamma(I)/\Gamma(HI^+) \quad (2)$$

where $\gamma(I)$ and $\gamma(HI^+)$ are the activity coefficients of the non-protonated and protonated forms of indicator and $\Gamma(I)$ and $\Gamma(HI)$ is the transfer activity coefficient from water to the PIL.

For a very dilute solution of indicator, the ratio of the activity coefficient of the protonated and non-protonated forms of indicator remains constant. The ratio of the transfer activity coefficient of the two forms of indicator depends on their solvation. This difficulty can be resolved by assuming that this ratio is unity and does not depend on the choice of the solvent. However, it is difficult to meet this demand, as different solvents solvate these two forms of the indicator to different extents. In the case of the structurally similar indicator molecule, it can be assumed that this ratio remains constant.

The acidity determination in binary mixtures involving pure ILs has been carried out by the same method as used in the case of pure PILs and water (Table S1, see Supporting Information). The mole fraction varies between $x_{\text{IL}} = 0$ and 1. The temperature dependent Hammett function can be obtained by using a Peltier which controls the temperature within an accuracy of ± 0.01 K.

RESULTS AND DISCUSSION

In order to obtain the acidity, a suitable and specific indicator is required. The $\text{p}K(I)_{\text{aq}}$ is a critical parameter for an indicator in

the acidity determination. The acidity level of a medium and its variation can be probed only by an indicator of suitable basicity ($\text{p}K(I)_{\text{aq}}$). An improper selection of indicator molecule will lead either to the disappearance of intramolecular charge transfer (ICT) spectra due to the protonation of indicator or to the protonation of water by added acid instead of protonating the indicator. Normally, in the case of strong acid, indicators having low $\text{p}K(I)_{\text{aq}}$ were found suitable. 2,4-Dinitroaniline is commonly used for strong acid ($\text{p}K(I)_{\text{aq}} = -4.53$) due to its much lower basicity. 4-Nitroaniline ($\text{p}K(I)_{\text{aq}} = 0.99$) and 2,5-dichloro-4-nitroaniline ($\text{p}K(I)_{\text{aq}} = -1.18$) always remained in protonated form when used for acidity determination of strong acids. The use of 2,4-dinitroaniline and 2,5-dichloro-4-nitroaniline for weak acid is also not very much effective, as the protonation level of indicator is noted as too weak and only a very small decrease in A_{\max} is observed during addition of acid. Therefore, an appropriate pairing between the basicity of indicator and the nature of acid is required before the measurement. On the basis of our observations, we selected 4-nitroaniline as a suitable indicator for acidity determination of weak organic acid.

The strength of an acid (acidity level) in a medium depends on the availability of proton (H^+) furnished by acid rather than the amounts of proton in strong acid.²⁸ The dilution of the acid shifts the acidity level from its original value. It was observed that all strong acids had a similar strength when the ratio of acid to water exceeded 1:6. However, this behavior was not expected during the dilution of weak acid because dissociation of weak acid prevailed over the solvation with an increase in dilution. However, it is interesting to observe the behavior of organic acids in water and PILs, as the interaction of proton is different in water from that in PILs. The relative order of acidity of HCOOH , CH_3COOH , and $\text{CH}_3\text{CH}_2\text{COOH}$ in water (Figure 3) and in four different PILs was observed opposite on the

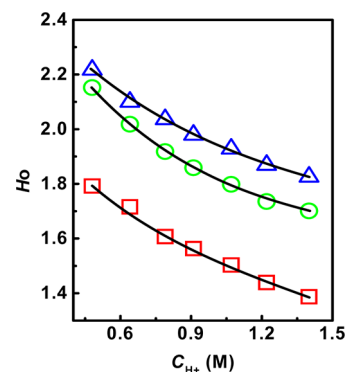


Figure 3. The H_0 vs C_{H^+} plots of HCOOH (red \square), CH_3COOH (green \circ), and $\text{CH}_3\text{CH}_2\text{COOH}$ (blue \triangle) in water.

Hammett scale, H_0 . The relative order of acidity in water was observed as



whereas the acidity order was reversed in all PILs shown in Figure 4 to summarize:



The values of H_0 for all PILs and the water system are given in Table 2. The H_0 for HCOOH is less in water than in PILs. However, the H_0 values for CH_3COOH and $\text{CH}_3\text{CH}_2\text{COOH}$ in PILs are obtained lower than that in water (see also Figure

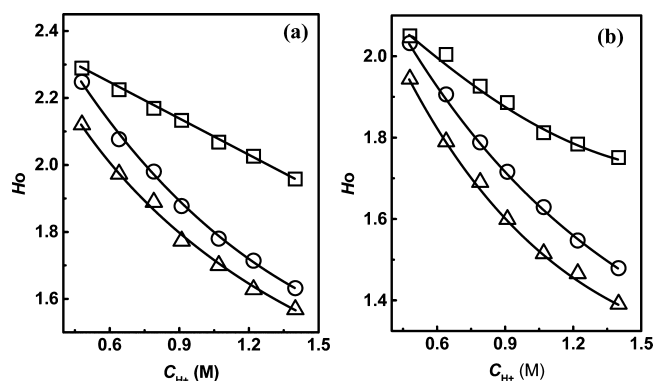


Figure 4. The Hammett function H_0 as a function of the acid concentration C_{H^+} for HCOOH (\square), CH₃COOH (\circ), and CH₃CH₂COOH (\triangle) in (a) [HmIm][CH₃COO] and (b) [HmIm][HCOO].

S2, Supporting Information). These observations for HCOOH, CH₃COOH, and CH₃CH₂COOH are very similar to those reported by MacFarlane et al. on different AILs having anions of variable basicity than water.²⁹ On the basis of their observations, they suggested that the relative basicity of water and IL anion is the controlling factor for the dissociation of acid. Thus, a highly basic anion promotes the dissociation of acid in an IL more than that in water and vice versa. Contrary to this, any of the PILs were observed to be sufficient to differentiate the organic acids in spite of the same anion. Thus, this assumption seems to be fairly applicable for predicting the acidity level in IL and water, but the acidity order of weak acids in a given PIL cannot be accounted for by using the same criterion. Therefore, the basicity of IL anion is only useful in classifying an acid more/less acidic as water. A more basic anion than water will always stabilize the acidic form of an indicator up to the same extent and vice versa. The different acidity values for organic acids in all PILs cannot be explained on

similar grounds. This indicates the involvement of PIL cation along with anion in the acidity determination. A detailed investigation on the acidity of weak acids in PILs having an anion of varying basicity should be helpful to reach any conclusion.

H_0 as a function of the molar concentration of acid (Figure 5) can be correlated by using a simple polynomial expression which is given as

$$H_0 = H_{0,C=0} + B_1 \cdot x + B_2 \cdot x^2 \quad (3)$$

where $H_{0,C=0}$ is the Hammett function at zero concentration, B_1 articulates the dependency of H_0 on concentration (x), while B_2 the unfavorable association of acid in the medium. B_1 is $-ive$ for all the PILs and the water system. It directly depends on the protonation of the indicator. A $+ive$ value of B_2 may be due to the association of acid molecule promoted by PIL and water (Table S2, see the Supporting Information).

A comparison of PILs in promoting the acidity either due to the change in anion or due to the increase in the alkyl chain length on the cation enables us to know about the structural variations that affect the H_0 values. From Figure 3, it is evident that the acidity level for all organic acids is maximum in [HmIm][HCOO] rather than in other PILs. This unique behavior of [HmIm][HCOO] in promoting acidity suggests a greater dissociation of acid in the medium, and this can be accounted for either because of the lower solvation of proton or the higher stabilization of conjugate base in the PIL.

Acidic behavior of an acid in a medium depends on the stabilization of its conjugate anion (X^-) by the medium.



Different H_0 values therefore indicate different levels of stabilization of anions [HCOO]⁻, [CH₃COO]⁻, and [CH₃CH₂COO]⁻ in water and in PILs. The different levels of anion stabilization may be either due to the structural differences between water and the PIL or due to the

Table 2. Hammett Function of HCOOH, CH₃COOH, and CH₃CH₂COOH in Water and PILs

water/PILs	organic acid	concentration (M)						
		0.48	0.64	0.79	0.91	1.07	1.22	1.40
H ₂ O	HCOOH	1.792	1.716	1.607	1.563	1.503	1.439	1.387
	CH ₃ COOH	2.152	2.018	1.918	1.859	1.798	1.735	1.701
	CH ₃ CH ₂ COOH	2.217	2.100	2.036	1.979	1.928	1.869	1.826
[HmIm][HCOO]	HCOOH	2.050	2.004	1.926	1.886	1.812	1.784	1.751
	CH ₃ COOH	2.032	1.906	1.788	1.716	1.629	1.547	1.479
	CH ₃ CH ₂ COOH	1.944	1.790	1.690	1.599	1.515	1.466	1.391
[HmIm][CH ₃ COO]	HCOOH	2.289	2.225	2.169	2.133	2.068	2.026	1.958
	CH ₃ COOH	2.248	2.077	1.980	1.877	1.780	1.714	1.632
	CH ₃ CH ₂ COOH	2.120	1.973	1.889	1.773	1.700	1.628	1.568
[HbIm][HCOO]	HCOOH	2.313	2.204	2.119	2.051	1.995	1.946	1.908
	CH ₃ COOH	2.235	2.042	1.919	1.815	1.735	1.663	1.591
	CH ₃ CH ₂ COOH	2.157	1.987	1.856	1.758	1.678	1.613	1.546
[HbIm][CH ₃ COO]	HCOOH	2.384	2.281	2.202	2.149	2.066	2.017	1.979
	CH ₃ COOH	2.264	2.076	1.946	1.852	1.779	1.705	1.629
	CH ₃ CH ₂ COOH	2.099	1.940	1.824	1.734	1.655	1.596	1.532
[HPyr][HCOO]	HCOOH	2.245	2.118	2.045	1.949	1.865	1.817	1.757
	CH ₃ COOH	2.194	1.981	1.837	1.727	1.641	1.558	1.479
	CH ₃ CH ₂ COOH	2.118	1.923	1.784	1.686	1.592	1.517	1.447
[HPyr][HCOO]	HCOOH	2.153	2.067	1.967	1.896	1.860	1.785	1.737
	CH ₃ COOH	2.178	1.984	1.832	1.734	1.637	1.561	1.476
	CH ₃ CH ₂ COOH	2.144	1.937	1.814	1.728	1.652	1.557	1.482

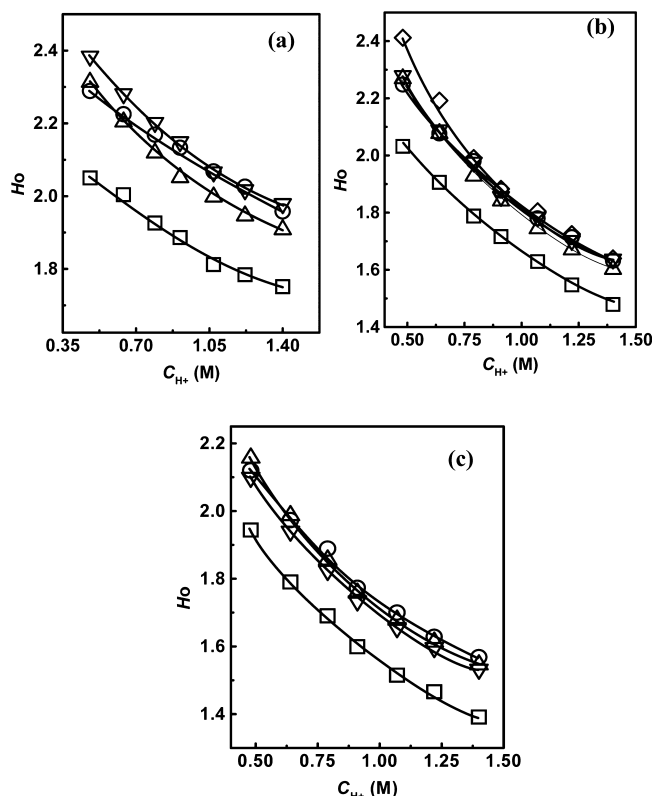


Figure 5. A comparison in the acidity of (a) HCOOH, (b) CH₃COOH, and (c) CH₃CH₂COOH in [HmIm][HCOOH] (□), [HmIm][CH₃COO] (○), [HbIm][HCOO] (△), and [HbIm][CH₃COO] (▽).

preferential stabilization of the anion by the medium. PILs are entirely different from water in structural aspects due to the presence of aromatic ring, alkyl chain, and Coulomb interactions between ions. It is, therefore, obvious that these structural features can influence the dissociation of organic acid. In order to confirm this, we plotted H_0 -H₂O vs H_0 -PIL for all three acids. A linear correlation between these two (Figure 6) confirms that the structural features of PILs do not influence the dissociation of acid or the protonation of the indicator and they act similar to water. However, the slope of linear correlation increases with the increase in the number of carbons in the acid molecule. This shows the higher

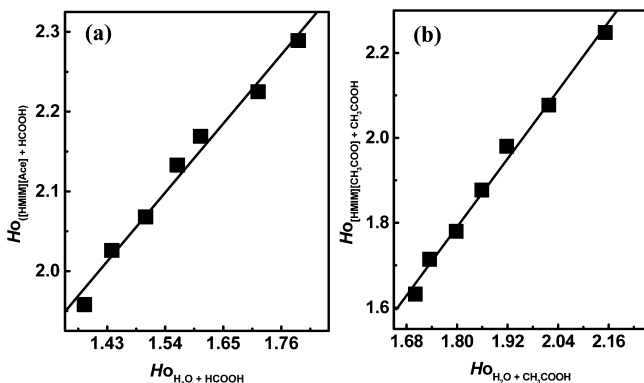


Figure 6. A linear correlation between H_0 -H₂O and H_0 -PIL for (a) HCOOH and (b) CH₃COOH.

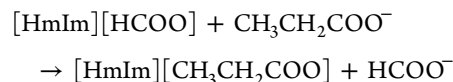
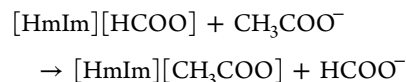
protonation of the indicator in PILs with the increase in the number of carbons in acid than in water.

Preferential stabilization of a conjugate anion of acid in a PIL favors the dissociation of acid, therefore influencing the acidity. The ratio between H_0 values of organic acids in water and in PIL, say, 1-methylimidazolium acetate, indicates the preferential stabilization by the PIL for higher carboxylic acid. In water, the ratio was observed as 1:1.20:1.24, while, in the PIL, it was 1.08:1.06:1 for HCOOH, CH₃COOH, and CH₃CH₂COOH, respectively. This reversal in H_0 ratio clearly indicates the preferential dissociation of CH₃COOH and CH₃CH₂COOH in the PIL. This preferential dissociation can be correlated by using Pearson's hard and soft acid base (HSAB) principle.³⁰

According to the HSAB principle, hard acid (low polarizability) binds preferentially with hard base and soft acid (high polarizability) binds with soft base. Carboxylic acids are weak acids, but their conjugate anion acts as a strong base. The relative hardness/basicity of carboxylate anions is in the order



The precursor of PILs, i.e., alkylimidazole, is a weaker base ($pK_a = 6.95$) than water ($pK_a = 15.7$). Transfer of a proton from carboxylic acid to alkylimidazole results in a strong conjugate acid. Since strong conjugate acid always prefers strong base, alkylimidazolium cation binds preferentially with the strongest base available. The preferential binding of alkylimidazolium cation follows the order of basicity of the anions. The exceptionally higher acidity level in [HmIm]-[HCOO] than other PILs can be explained as



Thus, a preferential binding of CH₃COO[−] and CH₃CH₂COO[−] anion with [HmIm]⁺ will shift the above equilibrium in the forward direction, therefore promoting the acidity. The steric effect due to −C₄H₉ inhibits the preferential binding of [HbIm]⁺ with basic anions in spite of the slightly lower basicity ($pK_a = 6.91$); therefore, the acidity in 1-butylimidazolium-based PILs was noted to be lower than that of 1-methylimidazolium-based PILs.

To ensure the validity of the above observations in determining the acidity order, we measured the H_0 in different classes of PILs having different cationic backbones combined with the HCOO[−] anion. The precursors of these PILs are 1-methylpyrrolidine ($pK_a = 10.55$) and 1-methylpiperidine ($pK_a = 10.08$). Therefore, the relative basicity order of their conjugate cations along with 1-methylimidazole ($pK_a = 6.95$) is



The relative stabilization of the conjugate anion of organic acids and hence the acidity order in these PILs are shown in Figure 7.

These plots reveal the influence of different PIL cations in determining the acidity level of organic acids due to preferential stabilization of the conjugate base of acids. Figure 7a strongly supports the involvement of favorable HSAB interactions

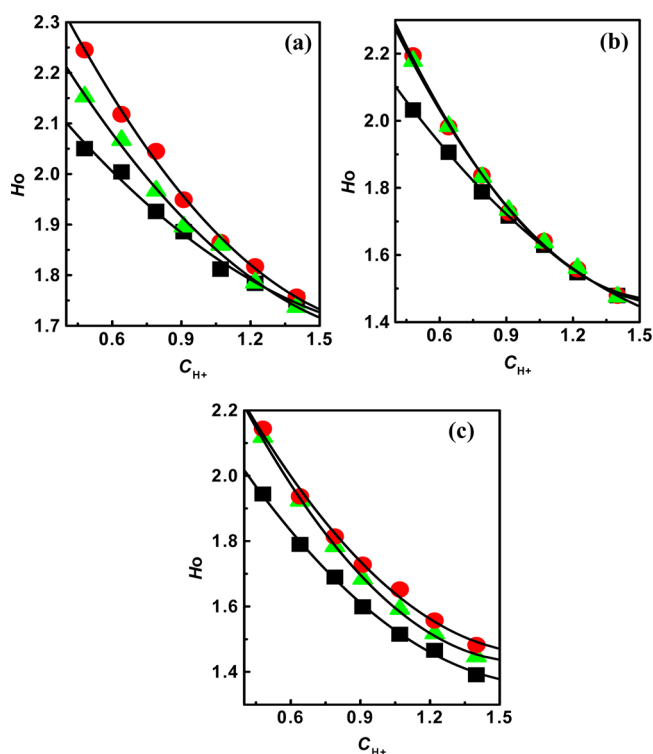


Figure 7. The acidity profiles of (a) HCOOH, (b) CH₃COOH, and (c) CH₃CH₂COOH in [HmIm][HCOO] (black ■), [HPyrd][HCOO] (green ▲), and [HPyrr][HCOO] (red ●).

between the PIL cation and the HCOO[−] anion. The acidity of HCOOH in these PILs was found according to the conjugate acidity of the PIL cation, as shown in eq 4. Figure 7b also indicates the favorable interactions *via* the HSAB principle. However, for CH₃COOH, the acidity order in [HPyrd][HCOO] and [HPyrr][HCOO] is not clearly differentiated in plots as compared to that for HCOOH. The H_0 value of CH₃COOH [HPyrd][HCOO] is slightly higher than that in [HPyrr][HCOO]. This anomalous behavior in the case of CH₃COOH may be due to the beginning of steric repulsion between the larger CH₃COO[−] anion and more crowded [HPyrd]⁺ than the less crowded [HPyrr]⁺ which in turn opposes the favorable HSAB interaction. Figure 7c further supports this view where steric repulsion completely dominates over HSAB interactions, and the acidity of CH₃CH₂COOH in [HPyrr][HCOO] was noted more than that in [HPyrd][HCOO] in spite of the higher conjugate acidity of [HPyrd]⁺ than [HPyrr]⁺. From the above evidence, it is obvious that, though HSAB interactions are the prime reason for the higher dissociation of organic acids in PILs, steric repulsion has a large and opposite influence on these favorable interactions.

The plots shown in Figures 3, 4, 5, and 7 were also drawn between H_0 versus $\log C_{H^+}$. We noted these plots to be linear with a unit slope (see the Supporting Information for a representative plot).

Temperature Dependent H_0 : The Activation Energy of Proton Transfer (E_{a,H^+}). PILs promote the acidity by making use of preferential binding; meanwhile, they may discourage the protonation of the indicator due to solvation. The thermal effect lowers the possibility of solvation, and it was observed that H_0 decreases with an increase in temperature, therefore increasing the availability of proton in the medium. Thermal effects alter the H_0 either due to the increase in thermal energy

of the solvated proton or the increase in the degree of dissociation of acid. Thermal effects also promote the dissociation of the protonated indicator into the aprotated form, therefore lowering the acidity (Figure 8). However, it was

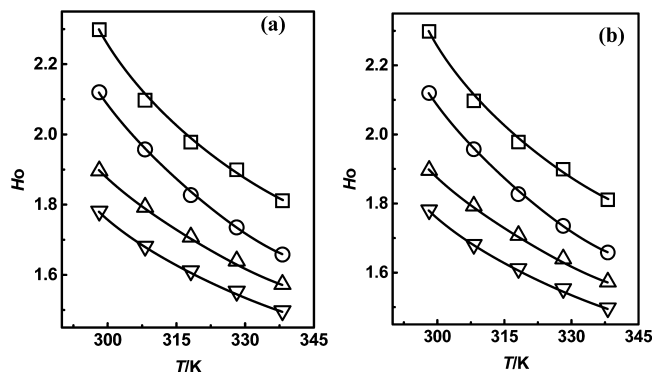


Figure 8. The H_0 – T plots for (a) HCOOH and (b) CH₃CH₂COOH in [HmIm][CH₃COO] at 0.48 M (□), 0.79 M (○), 1.07 M (△), and 1.4 M (▽).

assumed that such opposing phenomena have a very small contribution toward the H_0 value. The experimental temperature range for the thermal effect varies from 298.15 to 338.15 K.

From these plots, it is evident that H_0 decreases exponentially with temperature. This behavior is analogous to the k – T relation in kinetics and η – T relation in viscosity measurements, where the activation energy of reaction (E_a) determines the fate of the reaction and the activation energy of viscous flow (ΔG^\ddagger) determines the fluid behavior of liquid, respectively. On similar grounds, a medium can also affect the protonation of the indicator and, therefore, the H_0 value. Therefore, the use of an Arrhenius-type equation for the calculation of the activation energy of proton transfer E_{a,H^+} is desirable (Figure 9). E_{a,H^+} is the measure of the barrier caused

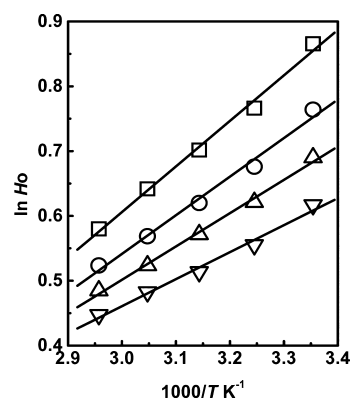


Figure 9. The Arrhenius-type plots for CH₃COOH in 1-methylimidazolium acetate at 0.48 M (□), 0.79 M (○), 1.07 M (△), and 1.4 M (▽).

by the medium, and it decides the extent of protonation of the indicator. The expression for the dependence of H_0 (for proton transfer) on temperature can be thought to follow an Arrhenius-type equation:

$$H_0 = (H_0)_0 e^{-E_{a,H^+}/RT} \quad (5)$$

where $(H_0)_0$ is the value of the Hammett function at room temperature, E_{a,H^+} is the activation energy of proton transfer, and R is the universal gas constant.

Taking the natural log of eq 5,

$$\ln H_0 = \ln(H_0)_0 - E_{a,H^+}/RT \quad (6)$$

The trend of change in H_0 values is different from the change in rate constant (k) with temperature. The plots of $\ln H_0$ vs $1/T$ are straight lines with a positive slope (E_{a,H^+}), opposite to that expected from eqs 5 and 6. This is due to the higher protonation of the indicator with a rise in temperature, which in turn decreases the H_0 value. Thus, eqs 5 and 6 are valid for the temperature dependent Hammett function. This validation of $\ln H_0$ vs $1/T$ opens the possibility of qualitative discussion about protonation of the indicator in terms of the activation energy of proton transfer (E_{a,H^+}). In a medium, the availability of a proton depends on the interaction of the proton with the medium, i.e., solvation. An increase in temperature favors the availability of a proton by weakening the proton–solvent interactions. The energy required to release the proton from the solvated form to the free form is equal to the activation energy of proton transfer (E_{a,H^+}). In PILs, E_{a,H^+} ranges from 4 to 12 kJ/mol. It was noted that the weakly solvated protons have a lower value of E_{a,H^+} , while strongly solvated protons have a higher E_{a,H^+} . These observations are in good agreement with the earlier reports based on the enthalpy of solvation (ΔH) of protons, according to which the availability of a proton in a medium and not the added concentration determines the acidity level.²⁸ In addition, thermal investigation of acidity function, H_R , and H_0 in water using aqueous sulfuric acid is reported.³¹

We also extend our experimental study to find the E_{a,H^+} values at various concentrations of acid (Figure 10). Our

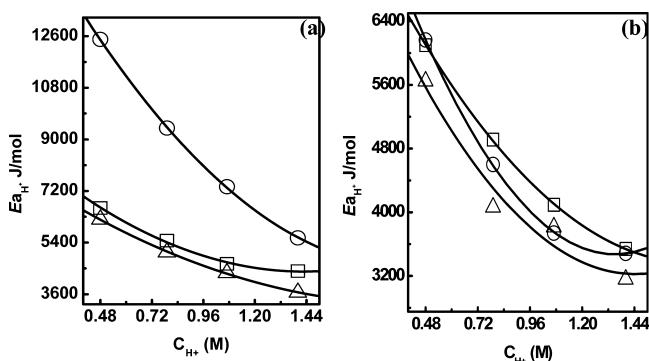


Figure 10. The E_{a,H^+} –concentration plots for HCOOH (\square), CH_3COOH (\circ), and $\text{CH}_3\text{CH}_2\text{COOH}$ (\triangle) in (a) $[\text{Hblm}][\text{HCOO}]$ and (b) $[\text{Hmlm}][\text{HCOO}]$.

observations are important because they respond to the curiosity: “Are the thermal changes equally effective for all the acids?” The previous discussion showed that the protons dissolved in a medium are more susceptible toward the thermal changes rather than the change in concentration of acid.

These drawings show that the acidity level of CH_3COOH in 1-butylimidazolium formate becomes more sensitive toward temperature with an increase in concentration. For HCOOH and $\text{CH}_3\text{CH}_2\text{COOH}$, the acidity level is less sensitive toward temperature with an increase in concentration. The above discussion is only valid about the availability of proton in the medium during a change in both concentration and temper-

ature. It, however, does not indicate the acidity order in the medium. The H_0 was observed to decrease or remain constant for HCOOH, while it decreased for CH_3COOH and $\text{CH}_3\text{CH}_2\text{COOH}$ with a rise in temperature. A very low E_{a,H^+} for HCOOH (-417 J mol^{-1}), CH_3COOH (103 J mol^{-1}), and $\text{CH}_3\text{CH}_2\text{COOH}$ (149 J mol^{-1}) suggests a lower protonation barrier in water than in PILs (Table S3, Supporting Information). A *–ive* value of E_{a,H^+} for HCOOH indicates that most of the indicator remains in protonated form and an increase in temperature further facilitates the protonation. The E_{a,H^+} values for CH_3COOH (852 J mol^{-1}) and $\text{CH}_3\text{CH}_2\text{COOH}$ (1240 J mol^{-1}) were observed less than in PIL, indicating an easy availability of proton with a rise in temperature; however, the observed H_0 values for CH_3COOH and $\text{CH}_3\text{CH}_2\text{COOH}$ were lower in PILs than in water. Thus, the selection of medium directs the protonation and hence influences the acidity level.

Acidity Level in Binary Mixtures of PILs in Water. A reverse acidity order of HCOOH, CH_3COOH , and $\text{CH}_3\text{CH}_2\text{COOH}$ in water and PIL encouraged us to find out the acidity level in a binary mixture of these two solvents. The recent studies in binary composition depict that the nature of solute–solvent interaction is completely different from that of the pure solvent.³² Any change in the composition of the solvation shell of solute by adding other solvents leads to a change in the property. The overall interactions between solvents either change the interactions between solute and solvent or result in a new medium called a “pseud solvent”. The pseud solvent having the properties of both of the solvents leads to an abrupt change in the magnitude of the properties as compared with that of the pure components. The purpose of this observation in binary mixtures is to locate the component that controls the acidity level, since both PILs and water are hyperpolar in nature. A polar solvent makes the dissociation easy and hence promotes the acidity level in binary mixtures. However, the outcome is quite interesting and indicates the participation of both a synergetic effect as well as preferential solvation. The dominance of the synergetic effect over preferential solvation and vice versa stems from the complex PIL–water–acid interaction. A detailed investigation using the deuterated NMR technique can be helpful to find out the real picture of this complex interaction. The scarcity of acidity models based on the Hammett function further makes understanding difficult. Earlier reports on binary mixtures show that the measured properties distribute between the pure components and they were found much higher than the pure component on certain occasions due to cooperative/synergetic behavior.³³ The deviation in measured quantities from the pure component may be positive/negative. The Hammett function for binary mixtures follows a similar trend. In addition, there are also some oddities in the observations that are discussed in detail.

The H_0 values for HCOOH in the binary mixture of all PILs were noted to increase, therefore decreasing the acidity level (Figure 11). A sudden increase in the H_0 value with addition of PILs suggests that PILs have a dominating role in determining the protonation of the indicator. However, the H_0 value in binary mixtures was noted to be higher than that of its pure components. Therefore, the generation of an intermediate solvent/pseud solvent is suspected to have a similar characteristic to the PILs. The effect of an intermediate solvent/pseud solvent on the H_0 value becomes intense, as the difference in the H_0 value of the pure component becomes low.

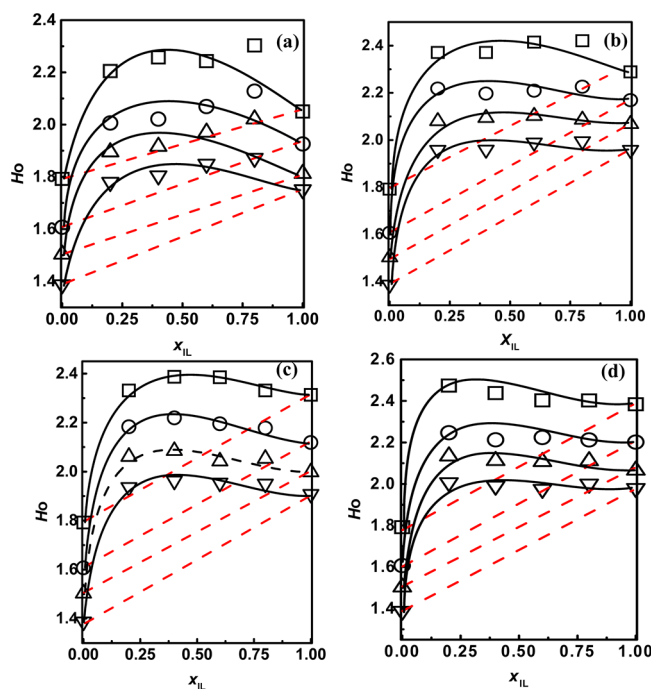


Figure 11. The plot of H_0 – x_{IL} for HCOOH in (a) [HmIm][HCOO], (b) [HmIm][CH₃COO], (c) [HbIm][HCOO], and (d) [HbIm][CH₃COO] at 0.48 M (□), 0.79 M (○), 1.07 M (△), and 1.4 M (▽). The dashed lines are shown to bring out the contrast from nonlinearity.

However, at a given composition of water and PILs, an increase in the concentration of acid lowers the magnitude of H_0 , therefore increasing the acidity level. This observation indicates the steady behavior of the pseudosolvent over all the concentrations of acid. The H_0 value for HCOOH shows a positive deviation. The magnitude of the deviation being higher than the pure component clearly indicates the synergetic behavior of pseudosolvent for HCOOH.

The H_0 values for the CH₃COOH in binary composition also reveal the presence of pseudosolvent that has similar characteristics to the PILs. However, except for the [HmIm][HCOO], all other PILs have a higher H_0 value for CH₃COOH than that of water (Figure 12). The relative H_0 value for water and PIL modifies the nature of the pseudosolvent, which influences the deviations in the H_0 value for binary mixtures.

In [HmIm][HCOO], the positive deviation at lower concentration of acid becomes negative with the increase in the concentration of acid. The reversal in the H_0 value indicates that the behavior of the pseudosolvent at lower concentration is similar to water, and at higher concentration, it behaves like the [HmIm][HCOO]. However, for other PILs, the change in the behavior of pseudosolvent appeared at higher concentrations. For [HmIm][HCOO], the H_0 value changes from positive to negative as the concentration of acid increases, therefore increasing the acidity level, while, for other PILs, a reversal in the nature from positive to negative is rarely observed. Unlike HCOOH, CH₃COOH has a lower positive deviation over the entire water–PIL compositions. Synergetic behavior of the pseudosolvent can only be witnessed where positive deviations take place. Evidently, it is clear that CH₃COOH is characterized by a higher acidity level than HCOOH in pure PILs and binary mixtures.

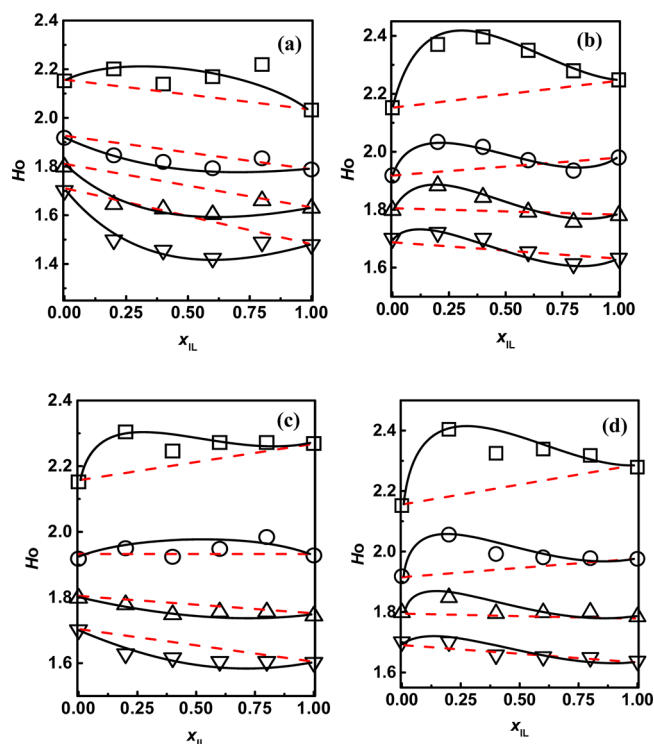


Figure 12. The plots of H_0 – x_{IL} for CH₃COOH in (a) [HmIm][HCOO], (b) [HmIm][CH₃COO], (c) [HbIm][HCOO], and (d) [HbIm][CH₃COO] at 0.48 M (□), 0.79 M (○), 1.07 M (△), and 1.4 M (▽). The dotted lines are shown to bring out the contrast from nonlinearity.

The H_0 values for CH₃CH₂COOH in all PILs are lower than those in water (Figure 13). Therefore, the characteristics of the pseudosolvent are similar to those of the PILs. However, it is also observed that the difference in H_0 value decides the deviation pattern with the rise in concentration of CH₃CH₂COOH. In [HmIm][HCOO], a large difference in H_0 value casts a permanent effect on the behavior of pseudosolvent and only the negative deviation in H_0 value is observed over the entire concentration change. The magnitude of this deviation is higher than that for other PILs. Thus, [HmIm][HCOO] is the most suitable PIL to promote the acidity in a binary mixture as well as in the pure state.

The other PILs show a positive deviation at lower concentration that becomes negative with the rise in the acid concentration. However, unlike positive deviation, where the synergetic feature of the pseudosolvent is common, in most of the PILs negative deviations are devoid of synergetic behavior, except for the [HmIm][HCOO], where a small decrease in H_0 value at $x_{IL} = 0.4$ was observed.

CONCLUSIONS

A detailed investigation on the acidity in PILs, their binary mixtures with water, and thermal effects on the protonation/deprotonation equilibria was carried out from which the following conclusions could be drawn:

(1) A reversal in acidity order of HCOOH, CH₃COOH, and CH₃CH₂COOH in water and PILs is observed. The higher acidity level of CH₃COOH and CH₃CH₂COOH in PILs is because of the preferential stabilization of the conjugate anion of acid with the cation of PIL according to the HSAB principle.

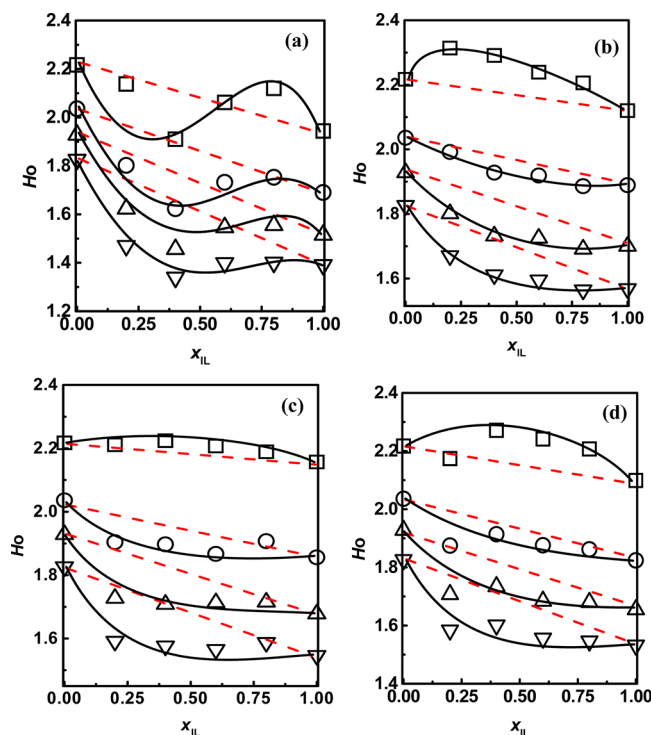


Figure 13. The plots of H_0 – x_{IL} for $\text{CH}_3\text{CH}_2\text{COOH}$ in (a) $[\text{HmIm}][\text{HCOO}]$, (b) $[\text{HmIm}][\text{CH}_3\text{COO}]$, (c) $[\text{HbIm}][\text{HCOO}]$, and (d) $[\text{HbIm}][\text{CH}_3\text{COO}]$ at 0.48 M (\square), 0.79 M (\circ), 1.07 M (\triangle), and 1.4 M (∇). The dashed lines are shown to bring out the contrast from nonlinearity.

(2) The increased steric hindrance can outplay the HSAB interaction.

(3) The thermal effect lowers the possibility of solvation during the protonation of the indicator. The activation energy of proton transfer, E_{a,H^+} , indicates the barrier provided by the medium during protonation/deprotonation equilibria.

(4) The H_0 value in the binary mixture clearly indicates the presence of an intermediate solvent/pseudosolvent. The behavior of pseudosolvent varies with the nature of acid and concentration. The synergistic characteristic of the pseudosolvent is more common for HCOOH and is rarely observed for CH_3COOH and $\text{CH}_3\text{CH}_2\text{COOH}$.

(5) The ability of the PILs to promote the acidity was noted to be higher in $[\text{HmIm}][\text{HCOO}]$ than other PILs.

The observations drawn above are expected to be useful in synthesizing an efficient IL for acid catalysis.

■ ASSOCIATED CONTENT

● Supporting Information

Additional drawings and tables regarding UV–visible spectra of 4-nitroaniline at different concentrations of acid, Hammett function calculation, acidity order of carboxylic acids, dependence of H_0 on concentration, change in the activation energy of proton transfer with concentration of acid, and a representative plot of H_0 versus $\log C_{H^+}$. 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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