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INFLUENCE OF THE HAMMETT BASE CONCENTRATION ON ACIDITY LEVELS IN IONIC LIQUIDS USING RAMAN SPECTROSCOPY AND HAMMETT ACIDITY FUNCTIONS

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Abstract

Room-temperature ionic liquids (RTILs) are a class of solvents with remarkable properties, including specific solvation properties and tuneable acidity levels. The Hammett acidity functions, commonly used to assess the acidity levels of ILs, rely on monitoring the protonation of colour indicators (especially nitroanilines) via UV-visible spectroscopy. However, this method possesses certain limitations, prompting our group to adapt it in Raman spectroscopy in a previous study. Yet the influence of the indicator concentration on the acidity functions has never been thoroughly examined. In this article, we investigated the effect of the 2,4-dichloro-6 nitroaniline concentration (from 7 to 50 mM) on the Hammett acidity functions estimated by Raman spectroscopy in 1-butyl-3-methylimidazolium bistriflimide, [BMIm]NTf$_2$. The acidity measured with this method was higher than the acidity evaluated via UV-visible spectroscopy but lower than the acidity evaluated via Strehlow acidity functions, suggesting specific solvation effects of the nitroaniline in [BMIm]NTf$_2$ and the formation of ion pairs in this solvent, which are discussed in this paper.

Keywords: Brønsted acidity, Hammett acidity functions, Hammett indicators, ionic liquids, Raman spectroscopy

Introduction

Ionic liquids (ILs) are a class of solvents that has attracted significant interest over the last few decades due to their attractive properties, such as low vapour pressure and low flammability. They are defined as organic salts characterised by a melting temperature below 100°C. Notably, room temperature ILs (RTILs) are liquid at or below room temperature, making them suitable solvents in a wide range of applications [1–3]. Today, common ILs are based on bulky and asymmetric cations (such as imidazoliums, pyridiniums and ammoniums) paired with weakly coordinating anions (such as hexafluorophosphate, $PF_6{}^-$, trifluoromethanesulfonate, OTf^- or bis [trifluoromethanesulfonyl] imide, $NTf_2{}^-$)[4]. Since their initial discovery in 1914 by Walden [5], followed by the pioneering works of Hurley and Weir [6, 7], Robinson and Osteryoung [8] and Wilkes et al. [9, 10], the number of ILs has significantly increased. Due to the vast number of possible cation-anion combinations (estimated to 10^6 by Plechkova and Seddon [11]), it is possible to design ILs with tailored properties for specific applications, which is why they are often referred to as 'designer solvents' [12]. Therefore, one of the remarkable features of ILs is that their chemicophysical properties can be adjusted according to their constituent ions, such as their viscosity, electrochemical window or solvation properties [13].

The solvation properties of the solvent towards the proton govern the acidity within ILs. For many chemical applications, the level of acidity achievable in ILs, often much higher than that accessible in water, turns out to be critical for reactivity and yet difficult to predict. For instance, acidic ILs are used in acid-catalysed reactions, such as Friedel-Craft alkylation, Fisher indole synthesis or the Mannich reaction [14]. They are also employed in battery and fuel-cell applications as well as in biomass valorisation, such as in lignin and cellulose depolymerisation [15].

A common method to assess the acidity of ILs is based on the Hammett acidity functions, developed by Hammett and Deyrup [16]. This approach relies on the protonation of weak bases in acidic medium, whose protonation equilibrium and the corresponding equilibrium constant are described by Equations (1) and (2), respectively, where a represents the relative activity, f the activity coefficient and c the concentration.

(1) $B + H^+ \rightleftharpoons BH^+$,

(2) $K_{BH^+} = \frac{a_{H^+} a_B}{a_{BH^+}} = a_{H^+} \frac{f_B}{f_{BH^+}} \frac{c_B}{c_{BH^+}}$.

Hammett and Deyrup defined their acidity functions H_0 by Equation (3).

(3) $\mathrm{H}_0 = pK_{BH^+} + \log\left(\frac{c_B}{c_{BH^+}}\right) = -\log\ (a_{H^+}) - \log\left(\frac{f_B}{f_{BH^+}}\right)$.

On the one hand, the acidity function is strictly equivalent to pH in diluted aqueous solutions of the base, as the activity coefficients of the base and its conjugated acid approach unity. On the other hand, Hammett postulated that the f_B / f_{BH^+} ratio remains constant for structurally related bases. Therefore, for a given medium, the acidity functions are independent of the base used. The family of Hammett bases, which was revised by Jorgenson and Hartter [17], is composed of primary nitroanilines, for which the pK_{BH^+} in water is determined.

Although the method was initially developed to measure the acidity of concentrated aqueous solutions of perchloric and sulphuric acids, it has been extended to nonaqueous solutions and is now recognised as a reference method to study the acidity of ILs. The first application of the Hammett acidity functions in ILs dates back to 1989 when Smith et al. [18, 19], followed by Osteryoung's group [20], investigated the acidity of HCl in the molten salt $AlCl_3$–1-ethyl-3-methylimidazolium chloride. In 2003, this acidity scale was extended to nonchloroaluminates ILs based on imidazolium cations paired with $NTf_2{}^-$ and $BF_4{}^-$ anions [21]. A few years later, the same group further expanded the scale to include OTf^-, $PF_6{}^-$ and $SbF_6{}^-$ anions [22, 23].

In nonaqueous solvents, the Hammett acidity functions are expressed by Equation (4), where the protonation equilibrium constant remains defined in water, but the ionisation ratio of the base (c_B/c_{BH^+}) is now considered in the solvent of interest [24]. The equation can be rewritten as Equation (5) by expressing the protonation equilibrium constant of the base, where Γ represents the transfer activity coefficient of the base and its protonated form from water to the nonaqueous solvent [24]. If the solvent s is water, then, as previously, the acidity functions are equivalent to the pH (for diluted solutions of the base). However, if s is a nonaqueous solvent, the acidity functions coincide with the pH in the solvent referred to the pH scale developed in water, assuming that the transfer activity coefficients of the base and its conjugated acid are equal (i.e., $\Gamma_B \,/\, \Gamma_{BH^+} = 1$).

(4) $$H_0 = pK_{BH^+,w} + \log\left(\frac{c_B}{c_{BH^+}}\right)_s,$$

(5) $$H_0 = -\log\left(a_{H^+,w}\right) - \log\left(\frac{\Gamma_B}{\Gamma_{BH^+}}\right)_w^s.$$

Finally, extrapolating the acidity functions for a standard solution of protons ($a_{H^+} = 1$) in the solvent s provides an estimation of $(\Gamma_{H^+})_w^s$, the transfer activity coefficient of the proton (Equation 6). This value reflects the difference between the origins of the pH scales in water and the nonaqueous solvent, as illustrated in Figure 1a. $(\Gamma_{H^+})_w^s$ is significant not only for determining this shift between the pH scales but also for accessing the solvation properties of the solvent towards the proton.

Indeed, the acidity that can be achieved in ILs is related to the solvation free energy of the proton in the solvent, $\Delta_{solv}G^\circ(H^+)_s$ [24, 25]. Although a consensus value for the proton solvation free energy in water, $\Delta_{solv}G^\circ(H^+)_w$, is known (−1112.9 kJ/mol) [26], this is not the case for ILs because its experimental determination is not straightforward. From the Hess cycle shown in Figure 1b, it is possible to assess $\Delta_{solv}G^\circ(H^+)_s$ by determining $\Delta_t G^\circ(H^+)_w^s$, the proton free energy of transfer from one solvent to another [25]. The latter is related to $(\Gamma_{H^+})_w^s$ by Equation (7), which is defined as the ratio of the relative activities of the proton in water $a(H^+)_w$ and in the nonaqueous solvent, $a(H^+)_s$ [24]. Therefore, Hammett acidity functions, using extrathermodynamic hypotheses, enable the determination of the proton solvation free energy in ILs through the H_0^0 value.

(6) $$H_0^0 = \lim_{a_{H^+,s}\to 1}\left(H_0\right) = -\log\left(\Gamma_{H^+}\right)_w^s,$$

(7) $$\Delta_t G^\circ\ (H^+)_w^s = RT\ln\left(\Gamma_{H^+}\right)_w^s = RT\ln\left(\frac{a(H^+)_w}{a(H^+)_s}\right).$$

Recently, the Hammett acidity functions were implemented for the first time in Raman spectroscopy in a previous study [27]. This technique offers several advantages, including greater flexibility in selecting the base acting as the pH probe, as noncoloured base can be deployed. Moreover, Raman spectroscopy can be used in coloured media, and the acidity functions can be correlated with measurements of proton coordination, also conducted via Raman spectroscopy, providing deeper insights in the local environment of protons in ILs. However, whether using UV-visible spectroscopy or Raman spectroscopy, the effect of base concentration on the acidity functions has never been investigated. Given that this probe is basic in the medium, it inevitably influences the accessible level of acidity in ILs, as already suggested by Robert et al. [22, 28]. This effect is particularly relevant in Raman spectroscopy, where the indicator concentration must be increased due to the lower sensitivity of the technique compared to UV-visible spectroscopy.

In this article, we analysed the influence of the basic probe concentration, 2,4-dichloro-6-nitroaniline, on the obtained acidity functions. The Hammett acidity functions were determined using Raman spectroscopy in 1-butyl-3-methylimidazolium bistriflimide, [BMIm]NTf$_2$, at several base concentrations, ranging from 7 to 50 mM.

Material and Methods

MATERIALS

1-Bromobutane (TCI Chemicals, 98%) was distilled once over di-phosphorus pentoxide (P_2O_5, VWR Chemicals, 98.2%). N-methylimidazole (Sigma Aldrich,99%) was distilled once under vacuum over potassium hydroxide (KOH, Merck, min 85%). Ethyl acetate (Fisher Scientific, $\geq$ 99.8%) and acetonitrile (Fisher Scientific, $\geq$ 99.9%) were distilled twice on P_2O_5. Dichloromethane (Fisher Scientific, $\geq$ 99.8%) was distilled once. Lithium bis (trifluoromethanesulfonyl)imide (LiNTf$_2$, TCI Chemicals, > 98%), bis (trifluoromethanesulfonyl)imide (HNTf$_2$, TCI Chemicals, > 99%) and 2,4-dichloro-6-nitroaniline (Aaron Chemicals, 98%) were used as received and transferred in a glovebox (atmospheric water content below 3 ppm) prior to use.

[BMIM]NTF$_2$ SYNTHESIS

An excess of 1-bromobutane was added dropwise in a round-bottom flask containing N-methylimidazole and acetonitrile. The system was placed under an argon atmosphere and was left to stir at room temperature for 24 h. The temperature was then raised to 60°C for another 24 h to complete the reaction. After 48 h, [BMIm]Br was crystallised by adding ethyl acetate, filtered and washed three times with cold ethyl acetate. Finally, it was recrystallised from a mixture of acetonitrile/ethyl acetate, filtered and dried under vacuum for at least 24 h. [BMIm]Br was obtained as a white solid.

[BMIm]NTf$_2$ was synthesised through anion metathesis between [BMIm]Br and LiNTf$_2$. Under an argon atmosphere, [BMIm]Br and LiNTf$_2$ were weighed and transferred to a round-bottom flask. Dichloromethane was added, and the reaction mixture was stirred at room temperature for 48 h. The white precipitate of LiBr was filtered and washed with cold dichloromethane. [BMIm]NTf$_2$ (contained in the filtrate) was purified using liquid–liquid extraction with small portions of triple-distilled water to extract the remaining LiBr from the organic phase. At each washing step, the aqueous phase was tested with $AgNO_3$ to detect the presence of LiBr. Once the test returned negative, two additional washing steps were performed. The purified [BMIm]NTf$_2$ was finally dried under vacuum for 5 days at 50°C to eliminate any traces of solvent.

PREPARATION OF ACIDIC SOLUTIONS OF 2,4-DICHLORO-6-NITROANILINE IN [BMIM]NTF$_2$

All solutions were prepared in a glovebox. 2,4-Dichloro-6-nitroaniline was dissolved in [BMIm]NTf$_2$ to reach the desired concentrations. From this basic stock solution, an acidic stock solution (150 mM in HTNf$_2$) was prepared by dissolving HNTf$_2$ in a fraction of the basic solution. Thereafter, less acidic solutions were prepared by mixing specific amounts of the basic and acidic stock solutions. As a result, all solutions of a given series had the same concentration of 2,4-dichloro-6-nitroaniline, but different concentrations of $HNTf_2$ (from 15 to 100 mM). A 1 M solution of $HNTf_2$ was also prepared from the basic stock solution to act as an acidic reference solution in which the indicator is fully protonated.

The standard error on the extrapolated value H_0^0 of the acidity functions was evaluated at two indicator concentrations (14.22 and 30.88 mM). From stock solutions of the indicator in [BMIm] NTf_2 at these two concentrations, three independent acidic stock solutions (150 mM in $HNTf_2$) were prepared, followed by three series of intermediate solutions (15–100 mM in $HNTf_2$). Three independent solutions in which the indicator was fully protonated (1 M in $HNTf_2$) were also prepared.

HAMMETT ACIDITY FUNCTIONS

The Raman spectrum of each solution was recorded (see section below), and the ionisation ratio of the colour indicator (c_{BH^+}/c_B) was determined through Equation (8), where I_B, I_{BH^+} and I are the intensities of the band of interest of the indicator in its fully deprotonated form, in its fully protonated form and partially protonated, respectively. The Hammett acidity functions at each $HNTf_2$ concentration (from 15 to 100 mM) were then calculated by Equation (9), knowing that the pK_{BH^+} of 2,4-dichloro-6-nitroaniline in water is −3.32.

$$(8)\ \frac{c_B}{c_{BH^+}} = \frac{I - I_{BH^+}}{I_B - I}$$

$$(9)\ H_0 = -3.32 + \log\left(\frac{I - I_{BH^+}}{I_B - I}\right)$$

RAMAN SPECTROSCOPY

Raman spectra were directly obtained in the solutions kept under argon atmosphere in crimp vials using a Labram 300 Raman spectrometer (Horiba) interfaced with a 532-nm DPSS laser (input power on the sample 40 mW) and with a 90° angle objective (Olympus 20x, N.A. 0.40). The Raman spectra were recorded in the Raman shift region from 800 to 1700 cm^{-1} with an acquisition time typically of a few seconds.

Data processing was performed using LabSpec 5 software (Horiba). Because the addition of $HNTf_2$ in the solutions led to a fluorescent background, the Raman spectra were baseline-corrected using a fourth-order polynomial over the entire range of Raman wavelength shift. The spectra were then normalised according to the 1020 cm^{-1} band (attributed to the ring elongation and N-Me stretching of the [$BMIm^+$] cation) [29]. The spectra of the basic solutions of the indicator at all studied concentrations (from 7.35 to 49.66 mM) are shown in Figure 2. The addition of the colour indicator in the solvent led to the appearance of two main bands at 851 and 1356 cm^{-1}, attributed to the Ar-NO_2 C-N stretching and nitro N=O symmetric stretching of the nitroaniline, respectively [30, 31]. The intensity of the band at 1356 cm^{-1} (being the most intense and from which the intensity of [BMIm]NTf_2 at the same position was subtracted) was used to compute the acidity functions according to Equation (8).

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Results and Discussion

The evolution of the Raman spectra of 2,4-dichloro-6-nitroaniline at 24.64 mM in [BMIm]NTf_2 as a function of the $HNTf_2$ concentration is shown in Figure 3a. As the concentration of acid increases, the intensity of the band at 1356 cm^{-1}, corresponding to the symmetric stretching of NO_2 (N=O) in the indicator, decreases due to the loss of resonance upon protonation of the aniline by acidic protons (added $HNTf_2$). However, these protons initially reacted with basic impurities (i.e., substances more basic than the probe) contained in [BMIm]NTf_2, such as imidazole or bromide ions from the IL synthesis or small traces of water [22, 28]. To determine the quantity of protons that first reacted with these impurities, the reciprocal ionisation ratio of the indicator (c_{BH^+}/c_B) was plotted against the $HNTf_2$ concentration in Figure 3b and extrapolated to 0, as explained elsewhere [27]. Here, the concentration of impurities is found to be 9.34 mM, which is subtracted to the $HNTf_2$ concentration for the determination of the acidity functions.

The Hammett acidity functions were then calculated for each acidic solution from Equation (8) and plotted as a function of the cologarithm of the $HNTf_2$ concentration (corrected for the basic impurities in the IL) in Figure 3c. The H_0 values can be fitted with a linear model (the slope was forced to 1 to follow the model of Hammett) and the extrapolation for a standard solution of protons in the solvent ($a_{H^+} = 1, y$ intercept of the regression) leads to $H_0^0 = -5.15 \pm 0.02$. This value indicates that for identical chemical potentials of protons in [BMIm]NTf_2 and water, their relative activity will be 5 orders of magnitude higher in [BMIm]NTf_2 than in water, leading to more negative values of pH in the IL, or, in other words, that the origin of the pH scale of [BMIm]NTf_2 corresponds to a pH of −5.15 in water.

The H_0 acidity functions were also calculated from series of acidic solutions in [BMIm]NTf_2 with varying concentrations of 2,4-dichloro-6-nitroaniline and are shown in Figure 4a. Again, according to the Hammett acidity functions equation, a linear model was fitted through the data and extrapolated to a unitary activity of protons to estimate the H_0^0 values, which are summarised in Table 1. The standard error associated with the estimation of the H_0^0 values is typically between 0.01 and 0.04 pH units, which is of similar amplitude with the standard error associated with experimental errors when the acidity functions are evaluated three times from three independent series of acidic solutions (all prepared from a single basic stock solution, to ensure a constant CI concentration for the three replicates). Indeed, the standard error associated with the H_0^0 values calculated from three independent series of measurements at two indicator concentrations, at 30.22 mM (middle of the tested concentration range) and at 14.88 mM (near the lower limit of the tested concentration range) was 0.01 H_0^0 units for both concentrations (see Figure S1).

Although the standard error on the estimated H_0^0 values appeared to be independent of the concentration of the CI in the range from 7 to 50 mM, the CI concentration influences the experimental values obtained for H_0^0. As shown in Figure 4b, where the H_0^0 values are plotted against the indicator concentration, the value for H_0^0 significantly decreases when the CI concentration decreases. As these values are obtained for a standard solution of proton ($a_{H^+} = 1$), the trend can only be related to the behaviour of the CI in the medium, where it acts as a weak base. Indeed, the CI is by nature more basic than the IL solvent.

As shown in Figure 4b, the H_0^0 values seem to be linearly correlated with the CI concentration. The H_0^0 value obtained for the series with the CI concentration of 7.35 mM is slightly deviating from the linear fit, yet not significantly (p value < 0.05). That shift might be due to the low Raman signals of the CI at low concentrations, where the signal at 1356 cm^{-1} is detected as a weak shoulder on the band from the IL's cation (at 1335 cm^{-1}), especially at high HNTf$_2$ concentrations as the CI signal is even weaker. This trend indicates that estimating the H_0^0 value for infinite dilution of the CI (i.e., the H_0^0 value that would be obtained for the standard solution of proton in the BMImNTf$_2$ without the interference of the basic CI) requires to determine the H_0^0 values using a series of CI concentrations and then extrapolate the value at a null concentration of CI. By doing so with our data, the extrapolated value was estimated to be H_0^0 = – 5.34 ± 0.04.

This $\left(\mathrm{H}_0^0\right)_0$value, determined using Raman spectroscopy, was compared with two analogues values that were experimentally estimated in [BMIm]NTf$_2$: the value of H_0^0 obtained using the Hammett acidity functions but determined by UV-Vis spectroscopy and the value $R_0^0\,(H^+)$ obtained using the Strehlow acidity functions determined by electrochemistry.

Indeed, the $H_0^0$was also estimated using UV-visible spectroscopy, which is the technique of reference for determining the Hammett acidity functions with coloured nitroanilines. In this work, three independent series of measurements (Figure S2) led to a value of H_0^0 = – 5.34 ± 0.04, which is consistent with the values reported in the same IL in former studies [22, 27]. This H_0^0 value is higher than our (H_0^0) value obtained by Raman spectroscopy, which was expected as $\left(\mathrm{H}_0^0\right)_0$should not be dependent on the basic behaviour of the CI in the medium, as discussed above. However, the H_0^0 value obtained by UV-Vis with a concentration of CI of only 1.51 mM corresponds to the H_0^0 value that would be measured by Raman spectroscopy with a solution containing ~20 mM of CI. Therefore, a shift of H_0 (and therefore of H_0^0) is observed when the Hammett acidity functions are estimated in the same medium, with the same probing CI, but two orthogonal techniques that are Raman and UV-visible spectroscopy.

A similar observation was made in a previous study examining the Hammett acidity functions of [HNEt$_3$]NTf$_2$-HNTf$_2$ mixtures using two colour indicators: 2,4-dichloro-6-nitroaniline and 2,4-dinitroaniline (pK_{BH^+} = −4.53) [22]. These two bases yielded to different H_0^0 values, contradicting Hammett's postulate, even though the same technique was used, that is, UV-vis spectroscopy. However, it was suggested that the shift of H_0 observed using two bases in the same medium is related to the formation of ion pairs between the indicator and the partially dissociated HTNf$_2$ acid (yet fully ionised), suggesting that the [BMIm]NTf$_2$ is not a dissociative solvent. Indeed, when ion pairs are formed with the CI and the acid, the change of colour of the probe is linked to the equilibrium given by Equation (10), rather than by Equation (1). This equilibrium leads to the apparent acidity function, described by Equation (11), which was first proposed by Brukenstein [32]. In this equation, $K_f^{BH^+X^-}$ represents the ion pair formation constant associated with the equilibrium in Equation (10). Therefore, our $\left(\mathrm{H}_0^0\right)_0$value, extrapolated for the solution where no CI is pres(ent, would be shifted from the H_0^0 value derived from UV-Vis measurements by pK_{BH^+} – log ($K_f^{BH^+X^-}$). If the pK_{BH^+} is known (value determined in the solvent, not in water), then the shift between both values enables to determine the extent of ion pairing in [BMIm]NTf$_2$. Unfortunately, no pK_{BH^+} value for the 2,4-dichloro-6-nitroaniline CI has been reported in [BMIm] NTf$_2$ in the literature.

(10) $B + HX \rightleftharpoons BH^+X^-$

(11) $$(H_0)_{app} = pK_{BH^+} + \log\left(\frac{c_B}{c_{BH^+X^-}}\right) = pK_{BH^+} - \log\left(K_f^{BH^+X^-}\right) - \log\left(c_{HX}\right).$$

Our $(H_0^0)_0$ value was also compared with the Strehlow acidity functions, $R_0^0\,(H^+)$ determined in [BMIm]NTf$_2$, based on the measurement of the electrochemical potential of the H$^+$/H$_2$ electrode. The extrathermodynamic hypothesis formulated by Strehlow suggests to use the redox couple ferricenium/ferrocene as a solvent-independent reference of potential [33]. Like the Hammett acidity functions, the Strehlow acidity functions are assimilable to a pH value expressed on the pH scale in water, and the $R_0^0\,(H^+)$ value, extrapolated for a standard solution of protons ($a_{H^+} = 1$) in the nonaqueous solvent, is equal to the shift between the pH scales of water and the nonaqueous solvent [24]. In a previous study [33], the $R_0^0\,(H^+)$ in [BMIm]NTf$_2$ was estimated to be −7.7, which is much more acidic than the extrapolated $(H_0^0)_0$ obtained here with Hammett acidity functions using Raman spectroscopy. However, the equality between R_0 and H_0 for a given acidic solution in a nonaqueous solvent is only met if the Hammett hypothesis that $\Gamma_B/\Gamma_{BH^+} = 1$ is verified. Therefore, this hypothesis is probably not met with nitroanilines, for which the strong acidity is due to the electron-withdrawing nitro group at the *para* position of the aromatic ring of the aniline, deployed in aromatic ILs such as [BMIm]NTf$_2$. One can expect pi-stacking to take place between the aromatic cation of the IL and the aromatic ring of the base, the force of which will vary according to the protonation state of the base because the electronic density on the aromatic ring is higher for the basic form of the CI. The difference between $(H_0^0)_0$ and $R_0^0\,(H^+)$ is then equal to $-\log\left(\frac{\Gamma_B}{\Gamma_{BH^+}}\right)$ [34] and is estimated here to be 2.1, indicating that the variation of the activity coefficient of transfer of the basic form of the CI from water to the [BMIm]NTf$_2$ is actually 2 order of magnitude lower than the variation of the activity coefficient of transfer of the acidic form of the CI.

Conclusion

For the first time, the influence of the colour indicator concentration used to determine the Hammett acidity functions was investigated. The acidity functions were determined in [BMIm]NTf$_2$ for a series of solution with increasing concentrations of HNTf$_2$, enabling to determine the H_0^0 value by extrapolation to a standard solution of protons $a_{H^+} = 1$, and with various concentration of the Hammett base, leading to a series of H_0 values. A linear model was fitted to estimate the H_0^0 value at null concentration of indicator, that is, the H_0^0 value that would be obtained for the standard solution of proton in the solvent without the interference of the basic indicator. This value, $\left(\mathrm{H}_0^0\right)_0 = -5.64 \pm 0.04$, seems to be a better estimate of the medium highest acidity accessible in the solvent, as acidity functions determined by UV-visible spectroscopy are shifted towards lower acidity levels (higher pH). Yet more experimental measurements of the Hammett acidity functions in the same solvent should be performed with different colour indicators, dissolved at different concentrations, to get more insights into the nondissociative behaviour of the solvent. A shift between the $\left(\mathrm{H}_0^0\right)_0$ obtained in Raman spectroscopy and the $R_0^0\left(H^+\right)$ obtained through electrochemical measurements of Strehlow acidity functions also indicates that the Hammett's hypothesis on the activity coefficients of the indicator and its protonated form might be invalid for nitroanilines in aromatic ILs. Further studies, relying on nonaromatic bases to determine the Hammett acidity function in ILs, are to be developed.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

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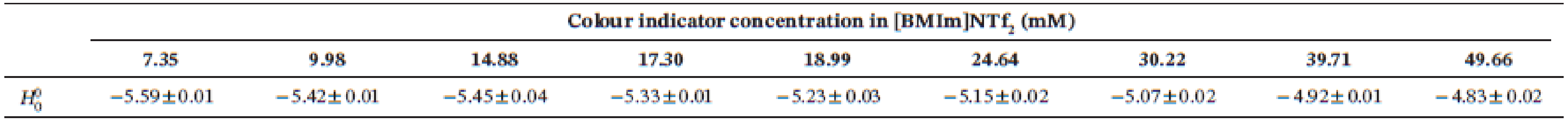
Table

Table 1. *H_0^0 values and their standard error obtained by Raman spectroscopy for various concentrations of 2,4-dichloro-6-nitroaniline in [BMIm]NTf₂. The standard errors indicate the error on the y intercept (H_0^0) of the linear regression performed in plots of H_0 versus the cologarithm of the HNTF2 concentration.*



	Colour indicator concentration in [BMIm]NTf$_2$ (mM)								
	7.35	**9.98**	**14.88**	**17.30**	**18.99**	**24.64**	**30.22**	**39.71**	**49.66**
H_0^0	-5.59 ± 0.01	-5.42 ± 0.01	-5.45 ± 0.04	-5.33 ± 0.01	-5.23 ± 0.03	-5.15 ± 0.02	-5.07 ± 0.02	-4.92 ± 0.01	-4.83 ± 0.02

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Figures

Figure 1. *(a) Correlation between the pH scales of water and a non-aqueous solvent.*pK_w*and* pK_s*are the self-ionisation constants of water and the nonaqueous solvent, respectively. (b) Hess cycle for the determination of the proton solvation free energy in a nonaqueous solvent starting from the proton solvation free energy in water and determining the proton transfer free energy from water to the nonaqueous solvent.*

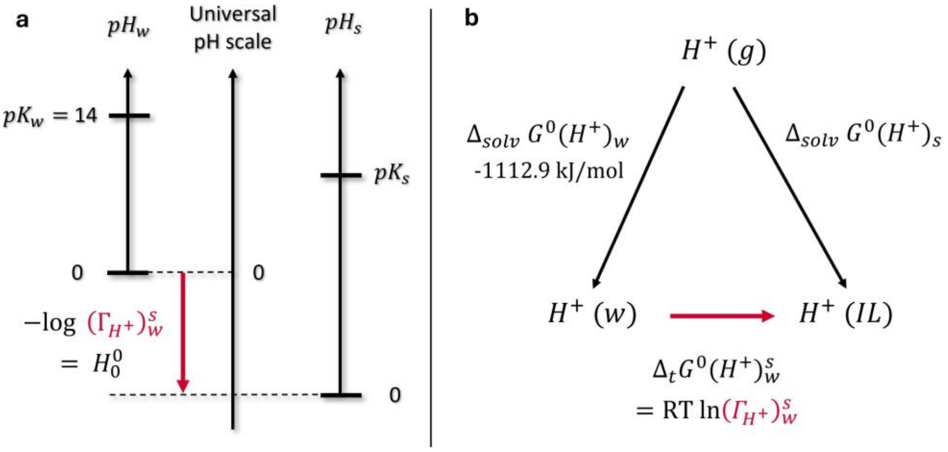

Figure 2. *Raman spectra of [BMIm]NTf₂ with increasing concentrations of 2,4-dichloro-6-nitroaniline (colour indicator), [CI] = colour indicator concentration. The dotted lines indicate the Raman bands specific to the colour indicator.*

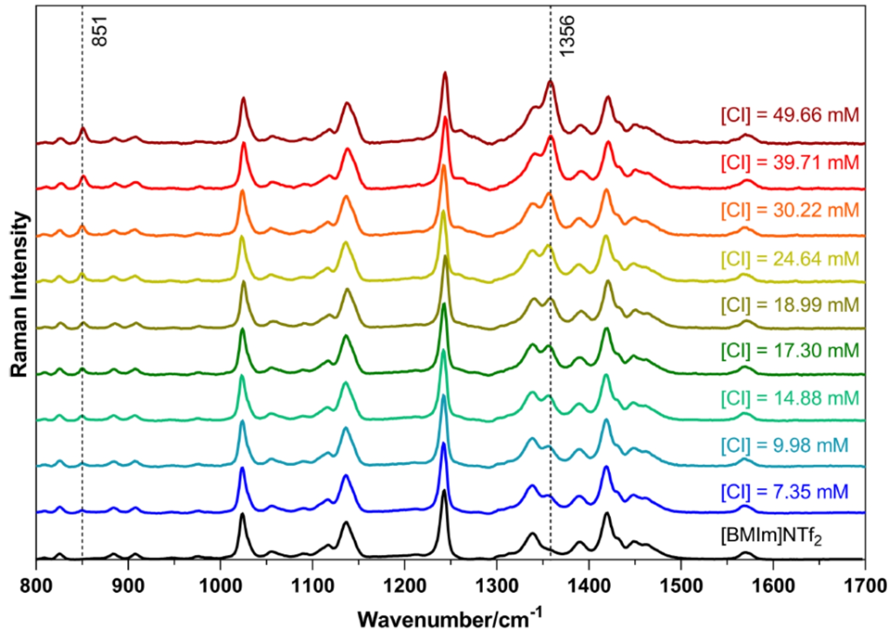

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Figure 3. *(a) Raman spectra of 25 mM of 2,4-dichloro-6-nitroaniline in [BMIm]NTf$_2$ as a function of the HNTf$_2$ concentration added. The experimental and fitted spectra are represented as plain symbols and plain lines, respectively. (b) Evolution of the reciprocal ionisation ratio of the base as a function of the HNTf$_2$ concentration in the solution. (c) Hammett acidity functions as a function of the cologarithm of the HNTf$_2$ concentration (from which the concentration of basic impurities was subtracted).*

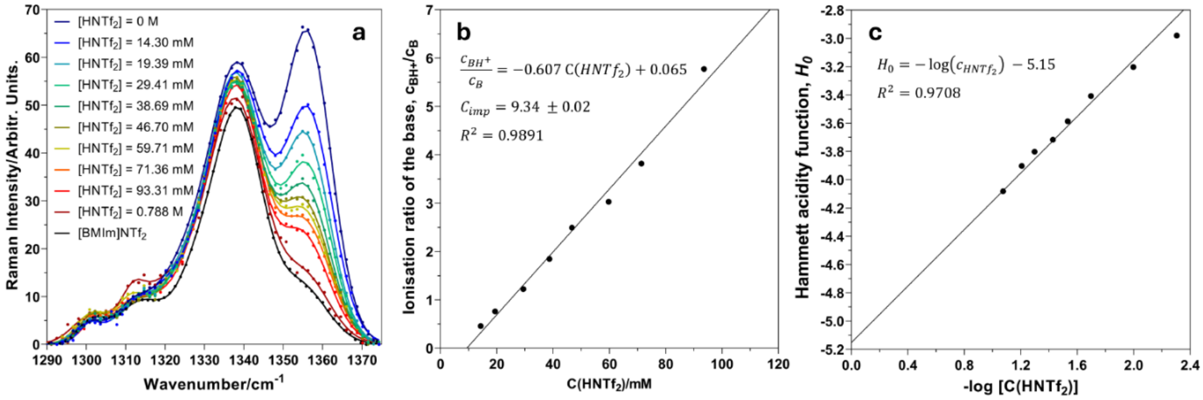
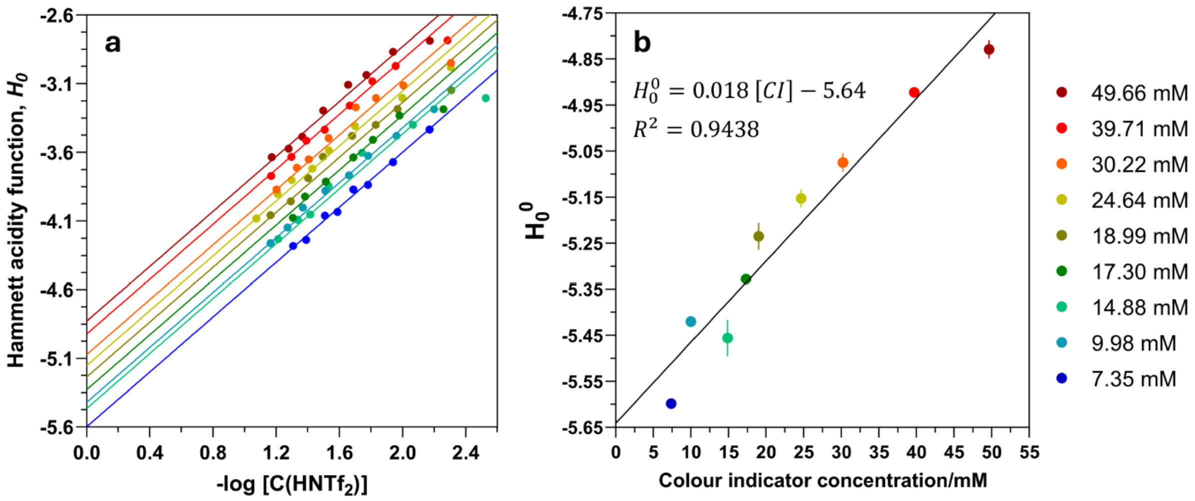


Figure 4. *(a) Hammett acidity functions as a function of the cologarithm of the HNTf$_2$ concentration (from which the concentration of basic impurities was subtracted) for all probed colour indicator concentrations. (b)* H_0^0*values obtained as a function of the probe concentration in [BMIm] NTf$_2$. The error bars indicate the standard error obtained on the* H_0^0*value from the linear model applied in plots of* H_0 *versus the cologarithm of the HNTF$_2$ concentration.*



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