

Synthesis, Characterization, and Spectroscopic Investigation of Anthranilic Acid Ionic Liquids

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Abstract: In this study, the synthesis and characterization of a series of new ionic liquids are achieved. The synthesis of ionic liquids was obtained *via* the acid-base neutralization reaction. The acid-base neutralization reaction was carried out by the reaction of anthranilic acid with tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide in water individually. The resulted products of ionic liquids were in good yield and purity. The ionic liquids are characterized by use of ¹H NMR spectroscopy, thermal gravimetric analysis, UV-Vis spectroscopy, and fluorescence spectroscopy. The obtained results using ¹H NMR analysis were in a very good agreement with chemical structure of synthesized ionic liquids. In addition, the results of thermal gravimetric analysis suggested that these ionic liquids have good thermal stability. Both Fluorescence and UV-Vis spectroscopy measurements provided that these ionic liquids have the same spectral profile. Time-based fluorescence steady-state measurements also showed that these ionic liquids have a high photostability.

Keywords: Ionic liquids; anthranilic acid; acid-base neutralization reaction; fluorescence; photostability.

Introduction

Ionic liquids (ILs), known as room temperature ionic liquids (RTILs), are salts with melting points below room temperature and a class of organic salts. ILs resemble molten ionic melts of metallic salts, constituting an organic cation with delocalized charge and a bulky inorganic anion^[1]. Both ILs and molten salts are composed of ions. The presence of bulky organic cations in ILs interrupts the crystal packing and lowers the melting temperature. ILs have a continual concern in environmental areas because of their potential as greener

solvent for many organic, inorganic, and polymeric substances as compared to conventional environmentally damaging organic solvents^[2]. Furthermore, these molecules have good thermal stability, variable viscosity, no effective vapor pressure, and recyclability^[3,4].

ILs have been widely used in several applications. For example, conventional organic solvents have been replaced by ILs in organic synthesis^[5,6]. They have been also used in solvent extractions^[7], liquid-liquid extractions^[8-10], enzymatic reactions^[11,12], electrochemical studies^[1,13,14], dye-sensitized solar cells^[15], as buffer additives in capillary electrophoresis^[16,17], as stationary phases in gas-liquid chromatography^[18,19], and as ultralow volatility liquid matrixes for matrix-assisted laser desorption/ionization (MALDI) mass spectrometry^[20,21].

Recently, there has been a large focus on the effectiveness of ILs as environmentally friendly, “green” solvents and as a host of practical applications to which they are amenable^[22,23]. In addition, understanding the mechanism and solvation in ILs is a difficult and challenging task because of its complex nature^[24,25]. Several studies have focused on this topic and a series of analytical techniques have been applied to explore the properties of these novel media^[26-30]. Most of analytical methods involve fast atom bombardment (FAB) mass spectrometry^[31], X-ray crystallography^[32], and X-ray absorption fine structure (XAFS)^[33]. These methods have shown considerable promise in studying the physicochemical properties of RTILs. However, problems have been encountered with some of these techniques. For example, ILs introduce significant problems, such as, their ability to dissolve most media, the production of uniform vertical liquid films, and the high levels of absorption/self-absorption when using XAFS.

On the other hand, electronic absorption and fluorescence techniques have shown considerable promise in studying the photophysical properties of RTILs. Fluorescence spectroscopy is one of widely used, dominant, and powerful methods for obtaining information on the structure and function of many molecules^[34]. However, the optical properties of RTILs have not been carefully investigated even though the optical behavior of a considerable number of dissolved solutes in the presence of these RTILs has been studied.

In accordance, synthesis and characterization of a series of new ILs were achieved in the present study. Characterization of synthesized ILs was carried out by use of ¹H NMR and thermal gravimetric analysis. Furthermore, steady-state fluorescence measurements of these ILs were performed, allowing for a deeper mechanistic understanding of ILS.

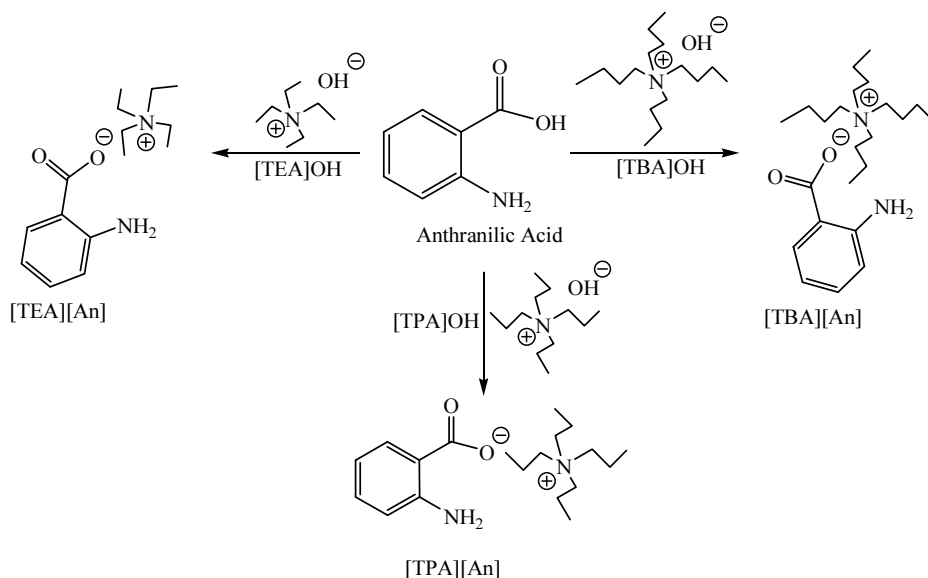
Experimental Section

Materials and Reagents

Anthranilic acid, tetraethylammonium hydroxide ([TEA]OH), tetra propylammonium hydroxide ([TPA]OH), tetrabutylammonium hydroxide ([TBA]OH), and sodium sulphate (Na_2SO_4) were obtained from Sigma-Aldrich (Milwaukee, WI) and used as received.

Synthesis Procedures

An aqueous solution of the desired base ([TEA]OH, [TPA]OH, or [TBA]OH), 14.58 mmol, was added to an equimolar amount of an aqueous suspension of anthranilic acid (14.58 mmol). The two solutions were mixed, stirred, and heated for 2 h. Water was removed under vacuum at 80 °C. The resultant residue was dissolved in acetonitrile (50 mL) and filtered for removing the unreacted amount of anthranilic acid. The filtrate was dried over Na_2SO_4 and filtered. The desired products of [TEA][An], [TPA][An], and [TBA][An] were finally obtained by removing the solvent under vacuum (Scheme 1).



Scheme 1. Synthesis of [TEA][An], [TPA][An], and [TBA][An].

Sample Preparation

A stock solution of each ionic liquid was prepared individually in ethanol by first dissolving an appropriate amount of the ionic liquid. All stock solutions were stored in the dark at 4°C. For both fluorescence and UV-Vis spectroscopic

studies, a standard solution of 10 μ M from each ionic liquid was prepared by adding appropriate amounts of ILs stock solution.

Instrumental Methods

One-dimensional ^1H NMR spectra were acquired in the single-pulse mode on a Perkin Elmer 600 MHz spectrometer. All ^1H NMR measurements were recorded in CDCl_3 by use of tetramethyl silane (TMS) as an internal standard. Thermal gravimetric analyses (TGA) were recorded using a thermal analysis instrument TGA-7 HR V6.1A (module TGA 1400 $^\circ\text{C}$). The thermal decomposition temperature (T_{dec}) of ILs was determined at a heating rate of 5 $^\circ\text{C}$ min^{-1} under nitrogen from 20 to 600 $^\circ\text{C}$. The UV/Visible absorption measurements were performed by use of a Perkin-Elmer UV-Vis scanning spectrophotometer. Absorption spectra were recorded at room temperature using a 10 mm quartz cuvette. Fluorescence measurements were also acquired using a Perkin-Elmer luminescence spectrofluorometer equipped with a 20-KW for 8 μs duration xenon lamp and gated photomultiplier tube (PMT) and/or red-sensitive R928 PMT detectors. All fluorescence measurements were collected at room temperature. The ILs emission spectra were recorded in a 10 mm quartz fluorescence cuvette with slit widths set for entrance and exit bandwidths of 5 and 5 nm on both excitation and emission monochromators, respectively. Fluorescence emission spectra of ILs were monitored at 325 nm excitation wavelength. All fluorescence spectra were blank subtracted before data analysis. For the photostability study of ILs, time-based fluorescence steady-state measurements were applied with excitation band pass set at 15 nm and emission band pass at 5 nm in order to enhance the photo bleaching. Time-based experiments were excited at 325 nm and monitored at 406 nm emission wavelength. The fluence level of the excitation source was open for 30 min.

Results and Discussion

Characterization of ILs

Before obtaining the final products of ILs *via* acid-base neutralization reaction, the filtrates [TEA][An], [TPA][An] and [TBA][An] were yellow, orange, and dark brown in color, respectively. The final products of these ILs in this study were all solids, except for [TBA][An]. The resulted [TBA][An] was extremely viscous liquid at room temperature, which can be attributed to the fact that [TBA]OH is the strongest base as compared to [TEA]OH and [TPA]OH bases. This property of [TBA]OH can easily deprotonate the carboxylic acid moiety of anthranilic acid, resulted in the carboxylate salt. The tetrabutylammonium cation has a bulk nature, allowing it to decrease intermolecular attractions. Consequently, this can maximize the probability of obtaining a salt that is liquid at room temperature. The physical properties of these ILs are reported in Table (1).

Table 1: Physical Properties of [TEA][An], [TPA][An], and [TBA][An].
 The symbols *rt* and T_{dec} represent room and decomposition temperatures, respectively.

ILs Product	Color	State at <i>rt</i>	Yield (%)	T_{dec} (°C)
[TEA][An]	Yellow	Solid	58.23	150
[TPA][An]	Orange	Solid	68.89	160
[TBA][An]	Dark Brown	Viscous Liquid	75.60	220

^1H NMR spectra of ILs synthesized in this study were consistent with their chemical structure. In ^1H NMR analysis, there is also a clear evidence for the deprotonation of the free acid.

[TEA][An]. This resulted in solid crystals of 2.26 g (58.23 % yield). The TGA measurement of this ionic liquid gave a decomposition temperature (T_{dec}) of 150°C, as shown in Fig. 1. ^1H NMR δ 1.18 (t, 3H, CH_3), 2.00 (q, 2H, CH_2), 6.61 (m, 2H, ArH-4 & H-5), 7.24 (m, 3H, ArH-3 & NH_2), 7.86 (d, 1H, ArH-6) ppm.

[TPA][An]. The product of this ionic liquid was also solid crystals of 3.24 g (68.89 % yield). This ionic liquid was thermally stable up to 160°C (Fig. 1). ^1H NMR δ 0.75 (t, 3H, CH_3), 1.35 (m, 2H, CH_2), 2.85 (t, 2H, CH_2), 6.55 (m, 2H, ArH-4 & H-5), 7.20 (m, 3H, ArH-3 & NH_2), 7.87 (d, 1H, ArH-6) ppm.

[TBA][An]. This resulted in an extremely viscous ionic liquid 4.17 g (75.60 % yield). The decomposition temperature (T_{dec}) obtained by TGA measurement of this ionic liquid was found to be 225 °C (Fig. 1). This indicates the T_{dec} of [TBA][An] was the highest in comparison to [TEA][An] and [TPA][An]. This can be due to the length of carbon chain of the selected base. [TBA][An] has the longest carbon chain as compared to [TEA][An] and [TPA][An]. In addition, a close examination of Fig. 1 shows that the thermal stability of these ionic liquids increased with an increase in the length of carbon chain of the selected base. ^1H NMR 0.80 (t, 3H, CH_3), 1.23 (m, 2H, CH_2), 1.39 (m, 2H, CH_2), 3.00 (t, 2H, CH_2), 6.58 (m, 2H, ArH-4 & H-5), 7.17 (d, 1H, ArH-3), 7.37 (s, 2H, NH_2), 7.94 (d, 1H, H-6) ppm.

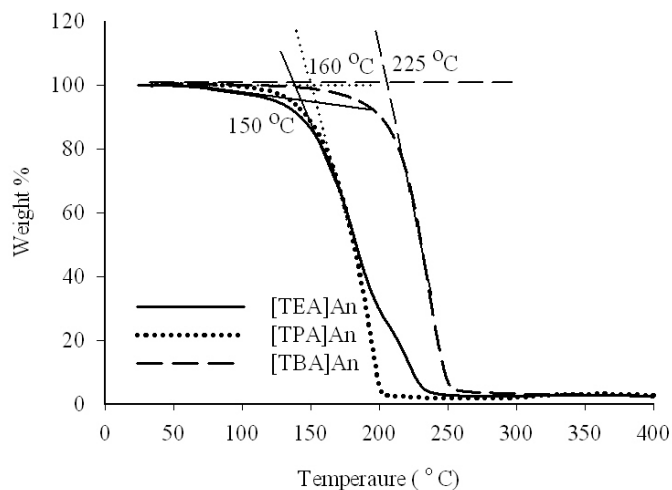


Fig. 1. Thermal gravimetric analysis of [TEA][An], [TPA][An], and [TBA][An], obtained with a heating rate of $5^{\circ}\text{C min}^{-1}$ under nitrogen from 20 to 600°C .

Spectroscopic Investigation of ILs

Fluorescence and UV-Vis Spectroscopic Studies

In order to compare these ILs with each other, both fluorescence emission and UV-Vis absorption spectra of ILs in this study were all collected at the same experimental and instrumental conditions (Fig. 2a-c and 3a-c). A close examination of Fig. 2a-c indicates the ILs have the same spectral profile in fluorescence emission spectra. Similar findings were also observed in UV-Vis absorption spectra of these ionic liquids (Fig. 3a-c). This is expected since all synthesized ILs only differ in the length of carbon chain of the selected base.

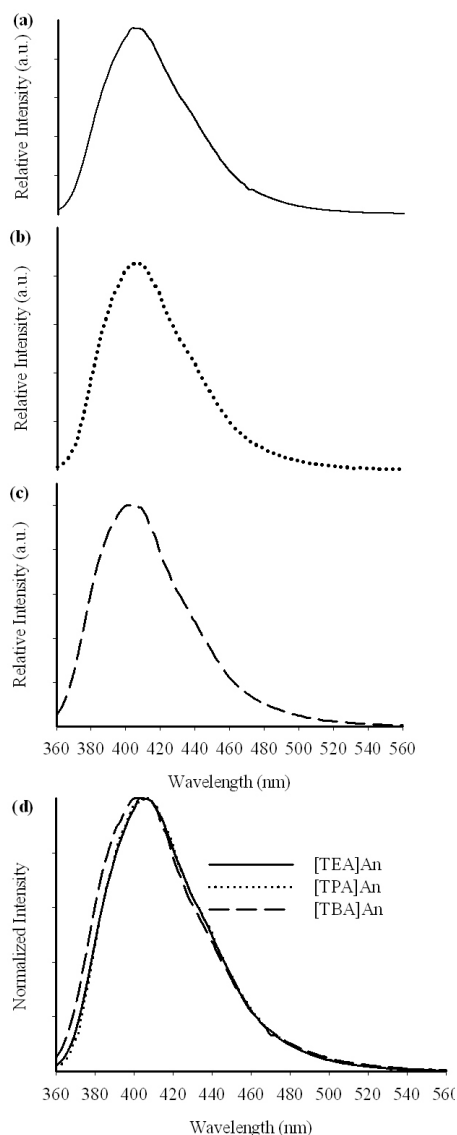


Fig. 2. Fluorescence emission spectra of 10 μM (a) [TEA]An, (b) [TPA]An, and (c) [TBA]An in ethanol, excited at 325 nm. (d) Normalized emission spectra of [TEA]An, [TPA]An, and [TBA]An.

However, there was a blue shift in the normalized fluorescence emission spectrum of [TBA]An in comparison to those of [TEA]An and [TPA]An, as illustrated in Fig. 2d. This blue shift was also noted in the normalized UV-Vis absorption spectrum of [TBA]An, as displayed in Fig. 3d, indicating both fluorescence and UV-Vis absorption results are consistent with each other (Fig.

2d and 3d). This may be ascribed to the length of carbon chain of the selected base. The [TBA]An ionic liquid has the longest carbon chain as compared to other ILs investigated in this study. This is also supported by the fact that [TBA]An is an extremely viscous ionic liquid, while both [TEA]An and [TPA]An are solid. In addition, This ionic liquid was found to decompose at the highest decomposition temperature (225°C) in comparison to [TEA]An (150°C) and [TPA]An (160°C), as displayed in Fig. 1.

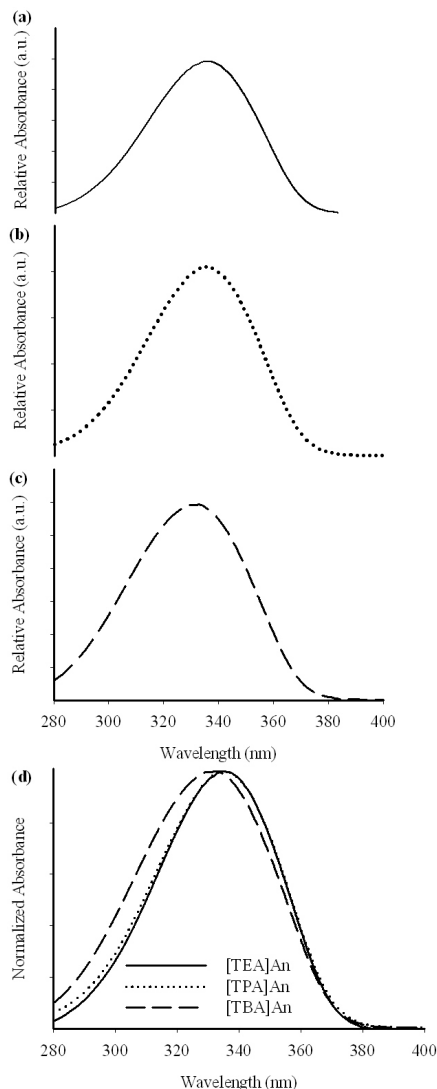


Fig. 3: UV-Vis absorption spectra of 10 μM (a) [TEA]An, (b) [TPA]An, and (c) [TBA]An in ethanol. (d) Normalized absorption spectra of [TEA]An, [TPA]An, and [TBA]An.

Photostability Study

In this study, time-based fluorescence experiments of all ILs were also obtained at the same experimental and instrumental conditions (Fig. 4). In addition, these measurements were obtained with the excitation bandpass set at 15 nm, and ILs have been exposed to radiation with an exposure time of 30 min in order to induce the photobleaching.

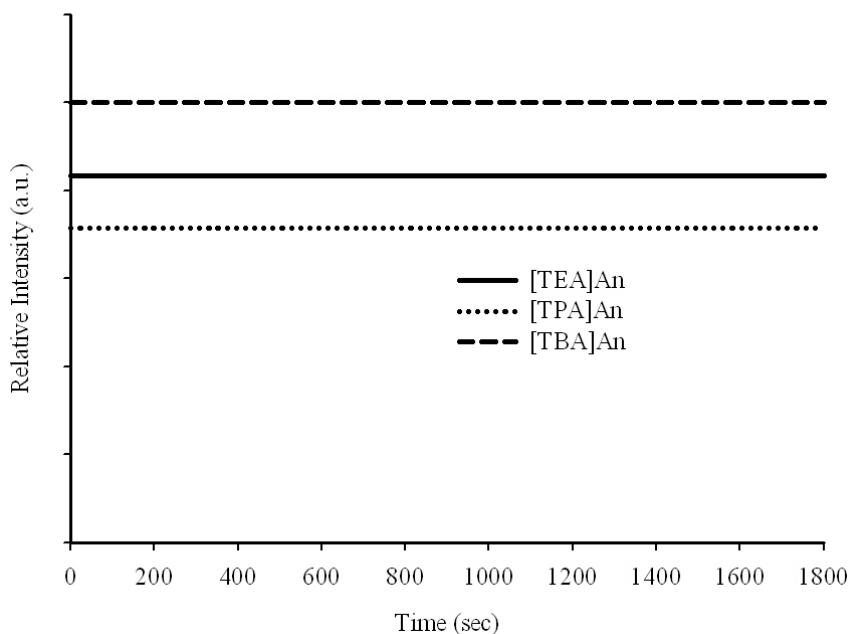


Fig. 4. Time-based fluorescence steady-state measurements of 10 μM [TEA]An, [TPA]An, and [TBA]An in ethanol, excited at 325 nm and monitored at 406 nm emission wavelength.

However, there was no decrease in the fluorescence intensity of all ILs with an increase in the time, as displayed in Fig. 4. This suggested that these ILs have a very high stability against photobleaching. The study of photostability is also consistent with data obtained from the decomposition temperature study of ILs, indicating their high thermal stability.

Conclusions

In this study, a straightforward route and a successful characterization of a series of novel ILs *via* acid-base neutralization reaction are achieved. The

products of these ILs were all solids, except for [TBA][An]. This ionic liquid is liquid at room temperature and has a high thermal stability. As a result, such compounds can be applied to high temperature reactions or gas chromatography. In addition, the resulted ILs are good absorbent, fluorescent, and have a very high photostability, as illustrated by spectroscopic studies. Finally, these ILs may also show considerable promise for using them in a range of applications, including biological and environmental.

Acknowledgement

King Abdulaziz University Research and Consulting Institute is thanked for its financial support. The author also thanks Prof. Hassan M. Faid-Allah for helpful discussions regarding this study.

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اصطناع وتوصيف وتحليل طيفي للمركبات السائلة الأيونية لحامض الإيثانيليك

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المستخلص: في هذه الدراسة، تم اصطناع، وتوصيف وتحليل طيفي لمركبات جديدة، من المركبات السائلة الأيونية لحامض الإيثانيليك. تم اصطناع هذه المركبات، باستخدام تفاعل تعادل الحامض مع القاعدة، بين حامض الإيثانيليك مع رباعي إيثايل أمونيوم هيدروكسيد، رباعي بروبايل أمونيوم هيدروكسيد ورباعي بيوتايل أمونيوم هيدروكسيد في الماء على حده. كما أنه تم الحصول على المركبات السائلة الأيونية بنسبة جيدة من الناتج والنقاوة. تم فحص هذه المركبات عن طريق الرنين النووي المغناطيسي للبروتون، والتحليل الوزني الحراري، وجهاز الأشعة المرئية وفوق البنفسجية الطيفي، وجهاز التألق الطيفي. النتائج التي تم الحصول عليها من الرنين النووي المغناطيسي للبروتون على توافق عالي مع الصيغة البنائية للمركبات السائلة الأيونية. بالإضافة إلى ذلك، أثبتت التحاليل الناتجة عن التحليل الوزني الحراري أن هذه المركبات تمتاز بثباتية حرارية جيدة. وتبين أن المركبات السائلة الأيونية لها نفس الانبعاث والامتصاص الطيفي، باستخدام جهاز التألق الطيفي، وجهاز الأشعة المرئية، وفوق البنفسجية الطيفي. كما أثبتت قياسات التألق الطيفي الزمنية أن هذه المركبات تمتاز بثباتية ضوئية عالية.