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Determination and correlation of the solubility of four Brønsted-acidic ionic liquids based on benzothiazolium cations in six alcohols

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ABSTRACT

Solubilities of four acidic ionic liquids based on benzothiazolium cations in six alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol) from at temperatures from (253 to 384) K were determined using a static equilibrium method under atmospheric pressure. The modified Apelblat equation and λh equation were employed to correlate the experimental data with good agreement. The solubilities of ILs increase with increasing temperature. It is interesting to find that the solubility of some ILs in alcohols are with "temperature-sensitive" properties. The solubility is related with the polarity and molecular structures of the solvent, as well as the strength of hydrogen bonding between alcohols and anionic groups of ILs. The dissolution enthalpy and entropy of ILs were calculated by the van't Hoff equation. This study provides useful information for further research and application of the ionic liquids.

1. Introduction

Ionic liquids (ILs) are low-melting salts, which consist of organic cations and smaller either organic or inorganic anions. In recent years, ILs have attracted tremendous attention due to their unique characteristics, which have simplified the manipulation and purification to facilitate the use in multiple reaction and extraction cycles [1,2]. Thus, various ILs have been synthesized and applied in some fields such as synthesis and extraction [3,4].

The physical and chemical properties of ILs are essential to their application. Herein, solubility is an important property for applications (*i.e.* separation, recovery and re-usage) of ILs. In the past few decades, ILs were utilized as catalysts for esterification and acetalization involving alcohols in many investigations [5,6]. Zhou and co-authors synthesized and employed acidic benzothiazolium ionic liquids to catalyse the esterification of benzoic acid and alcohols [7]. In addition, benzothiazolium ionic liquids were utilized as catalysts for acetalization of benzaldehyde and alcohols [8]. In these studies, the recovery of ILs is non-negligible work. Therefore, the solubility of ILs in alcohols is one of important factors affecting separation and purification of ILs from alcohols. Currently, the solubility measurements of ILs mostly focus on imidazolium and pyridinium ionic liquids [9–12]. With regard to the benzothiazolium ionic liquids, there have been fewer reports about the solubility data of ILs in alcohols until now.

In this work, four acidic benzothiazolium cations-based ILs were synthesized and their solubilities in six alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol) were measured with a static equilibrium method at different temperatures under atmospheric pressure. The relationship between structures and solubility of the four ILs is discussed. The experimental data were correlated with the modified Apelblat equation and λh equation, and the enthalpy and entropy of dissolution were determined based on the solubility results using the van't Hoff equation. The results could provide important information for further research and application of the ionic liquids.

2. Experimental

2.1. Materials and reagents

Referring to the previous literature [7], the four acidic benzothiazolinm cations-based ILs with mass fraction greater than 0.99 were prepared as follows: benzothiazole (CAS Number 95-16-9) (50 mmol) was dissolved in 50 mL ethanol and placed in a round-bottom flask equipped with a magnetic stirrer. The solution was cooled to temperatures between (273.15 and 278.15) K in an ice bath and 20 mL of an ethanol solution of methanesulfonic acid (CAS Number 75-75-2) (trifluoromethanesulfonic acid (CAS Number 1493-13-6); *p*-toluenesulfonic acid (CAS Number 104-15-4) or fluoroboric acid (CAS Number 16872-11-0) 60 mmol) was dropped slowly into the vigorously stirred mixture over a period of 0.5 h. The reaction mixture was continuously stirred for a further 4 h at room temperature. Ethanol was removed under vacuum

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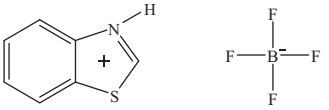
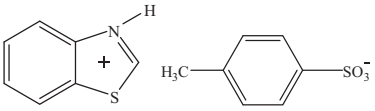
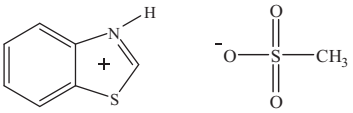
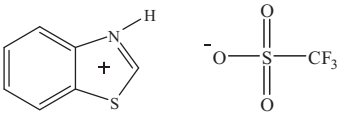
TABLE 1
Names, abbreviations, structures and melting temperatures of four acidic ionic liquids.[ab]

Names and abbreviations	Structures	T_{fus}/K
Benzothiazolium tetrafluoroborate [HBth][BF_4]		398.15
Benzothiazolium *p*-toluenesulfonate [HBth] [*p*-TSA]		393.15
Benzothiazolium methanesulfonate [HBth][CH_3SO_3]		378.15
Benzothiazolium trifluoromethanesulfonate [HBth][CF_3SO_3]		401.15

[a] The standard uncertainty u is u (melting point) = ±0.05 K.
[b] Standard uncertainty u was calculated using standard deviation (SD).

to afford crude ILs as white solid, which was washed three times with 10 mL diethyl ether. The crude ILs were purified by re-crystallization from hot ethanol to give colourless flake-like crystals, which were dried for 12 h under high vacuum at T = 353.15 K. The ionic liquids were characterized by a combination of ^{1}H NMR and ^{13}C NMR [7]. Their purity was determined by HPLC (LC-20AT, Shimadzu Corporation, Japan). The melting points of the four ILs were measured by automated melting point apparatus (MPA100, Stanford Research Systems, America) and listed in table 1, together with the abbreviations and molecular structures of all four acidic ILs.

Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol, supplied by Hangjia Chemical Co., Ltd. (Chengdu, China), were with analytical reagent grade and their mass fraction purities were higher than 0.995. The provenance and purity of chemicals used are given in table 2.

2.2. Apparatus and procedure

The solubility data were measured by a static equilibrium method. For each measurement, an excess mass of ILs was added to the solvent in three-neck flask. The flask fitted with a submersible magnetic stirrer, was placed in the thermostatic bath (±0.05 K, Gongyi Yuhua Instrument Co., Ltd., China) at the desired temperature. The equilibrium cell was heated to a constant temperature with continuously stirring at least 2 h and the actual temperature was recorded. Then the stirring was stopped and the solution was kept still until the upper layer was clear. About 1 mL upper portion of the saturated solution was sampled to a previously weighed vial determined by electronic balance (±0.0001 g, Shang-

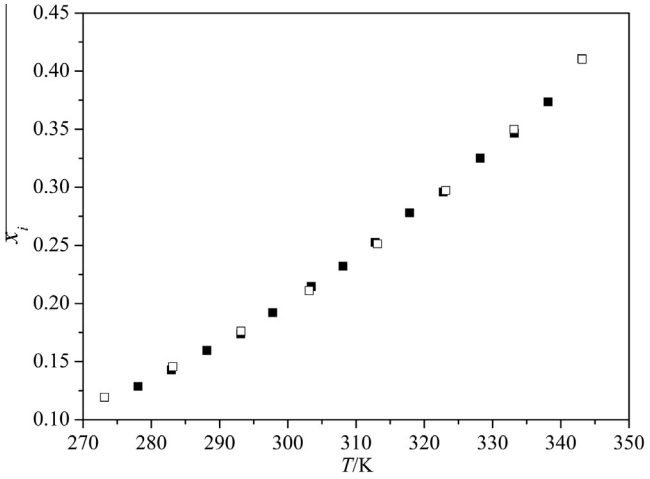


FIGURE 1. Solubility of benzoic acid in 2-propanol as a function of temperature: □, the experimental values; ■, the literature values.

TABLE 2
Provenance and purity of the chemicals used in this work.

Chemical used	Source	CAS registry number	Mass fraction purity by HPLC or GC	Method of purification
[HBth][BF_4]	Prepared in laboratory		⩾0.99	Method developed in our laboratory
[HBth][*p*-TSA]	Prepared in laboratory		⩾0.99	Method developed in our laboratory
[HBth][CH_3SO_3]	Prepared in laboratory		⩾0.99	Method developed in our laboratory
[HBth][CF_3SO_3]	Prepared in laboratory		⩾0.99	Method developed in our laboratory
Methanol	Chengdu Hangjia Chemical Co., Ltd.	67-56-1	⩾0.995	No further purification
Ethanol	Chengdu Hangjia Chemical Co., Ltd.	64-17-5	⩾0.995	No further purification
1-Propanol	Chengdu Hangjia Chemical Co., Ltd.	71-23-8	⩾0.995	No further purification
2-Propanol	Chengdu Hangjia Chemical Co., Ltd.	67-63-0	⩾0.995	No further purification
1-Butanol	Chengdu Hangjia Chemical Co., Ltd.	71-36-3	⩾0.995	No further purification
2-Methyl-1-propanol	Chengdu Hangjia Chemical Co., Ltd.	78-83-1	⩾0.995	No further purification