Suojiang Zhang · Qing Zhou
Xingmei Lu · Yuting Song
Xinxin Wang *Editors*

Physicochemical Properties of Ionic Liquid Mixtures

MATERIALS.SPRINGER.COM

Springer

Physicochemical Properties of Ionic Liquid Mixtures

Suojiang Zhang • Qing Zhou
Xingmei Lu • Yuting Song
Xinxin Wang
Editors

Physicochemical Properties of Ionic Liquid Mixtures

Springer

Editors
Suojiang Zhang
Beijing Key Laboratory of Ionic Liquids
Clean Process, Institute of Process
Engineering, Chinese Academy of Sciences
Beijing, China People's Republic

College of Chemistry and Chemical
Engineering, University of Chinese
Academy of Sciences
Beijing, China People's Republic

Xingmei Lu
Beijing Key Laboratory of Ionic Liquids
Clean Process, Institute of Process
Engineering, Chinese Academy of Sciences
Beijing, China People's Republic

College of Chemistry and Chemical
Engineering, University of Chinese
Academy of Sciences
Beijing, China People's Republic

Xinxin Wang
Beijing Key Laboratory of Ionic Liquids
Clean Process, Institute of Process
Engineering, Chinese Academy of Sciences
Beijing, China People's Republic

Qing Zhou
Beijing Key Laboratory of Ionic Liquids
Clean Process, Institute of Process
Engineering, Chinese Academy of Sciences
Beijing, China People's Republic

College of Chemistry and Chemical
Engineering, University of Chinese
Academy of Sciences
Beijing, China People's Republic

Yuting Song
Beijing Key Laboratory of Ionic Liquids
Clean Process, Institute of Process
Engineering, Chinese Academy of Sciences
Beijing, China People's Republic

ISBN 978-94-017-7571-7 ISBN 978-94-017-7573-1 (eBook)
DOI 10.1007/978-94-017-7573-1

Library of Congress Control Number: 2016954242

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer Science+Business Media B.V.
The registered company address is: Van Godewijckstraat 30, 3311 GX Dordrecht, The Netherlands

Preface

In the past two decades over 70,000 ionic liquid publications have been emerging, embracing a large number of physical chemical properties data. However, these hundreds of thousands of data are dispersed in more than hundreds of journals, reports, books and patent documents, which cause great difficulties for scientific researches and industrial applications. Therefore, it is imperative and necessary to collect those highly scattered data for providing comprehensive and systemic information. Professor Suojiang Zhang with his group is dedicating to such an important work for about 15 years, and published a handbook of pure ionic liquids entitled *Ionic Liquids: Physicochemical Properties* in 2009. In the present book, he attempts to present physicochemical properties data in particular for mixed systems, which are becoming more and more important with growing of the variety of functional ionic liquid systems and their applications.

This handbook featured not only abundant data but also measurement methods, fitting and prediction models. The work will be of huge value, on the one hand, it provides the possibility to extract common structure–property relationship information from various types of ionic liquids; on the other hand, it will provide indispensable information for validating the industrial practices based on ionic liquids. I hope that this work could play a fundamental role in stimulating and promoting more innovations in basic theories and industrial applications of ionic liquids, and finally contributing to the green dream of chemistry and chemical engineering.

Feb. 3, 2015 Mingyuan He
Beijing, China

Contents

Part I

Ionic Liquids Database

Ionic Liquids Database

1

1.1 Introduction

The nature of ionic liquids has been ‘hot’ with many attracted to study these remarkable substances which challenge our classical theory of the liquid state and provide opportunity for reform of traditional product engineering. In the past decade, as the research frontiers and focuses in the field of international green chemistry, its fundamental and applied research have made rapid progress, demonstrating their important scientific value and the huge potential application. Especially, ionic liquids have been designed as greener solvents to replace conventional volatile solvents and are showing increasingly promising perspectives in the diverse fields of synthesis, catalysis/biocatalysis, materials science, electrochemistry, and separation technology both at the laboratory and the industrial scale. For any kind of novel and promising substances, its basic and applied research exist side by side and play a part together; ionic liquids are no exception. With the persistent expansion and deepening of the application scope and level, the demand for the fundamental knowledge becomes more and more urgent, for instance, the properties and behavior law of correlative ionic liquids systems/mixtures in real engineering processes. Therefore, the reports on the properties of ionic liquids mixtures dramatically increased in just a few years, their total data points reached hundreds of thousands of properties data, including volume properties, transport properties, electrochemical properties, phase equilibrium, and so on. The above researches are very meaningful, which not only can obtain structure-activity relationship information to construct a new system of scientific theories but also have a certain role in promoting and facilitating for the related industrial development.

However, these hundreds of thousands of properties data have been dispersed in more than hundred kinds of international journals, reports, and patents. Therefore, it is necessary to collect, analyze data of all the properties of ionic liquids systems, and summarize laws, in order to adapt to the requirement of development and provide useful references for scientific workers. Derived from this original intention, we established the

S. Zhang et al., *Physicochemical Properties of Ionic Liquid Mixtures*,
DOI 10.1007/978-94-017-7573-1_1

original ionic liquids physicochemical properties database in 2004, updated annually, expanding from the pure ionic liquids to ionic liquids mixtures, and based on this database, we have made a series researches of structure-activity relationship.

A comprehensive database on physicochemical properties of pure ionic liquids and its mixtures, which has been collected from more than 1000 dependable literature sources in the period from 1982 to 2009, is available. There are more than 19,000 data points on the 29 kinds of physicochemical properties for 2311 available pure ILs, from which 907 kinds of cations and 229 kinds of anions were extracted. And there are more than 65,050 data points on the 39 kinds of physicochemical properties for 1388 mixture systems. These systems include 1047 binary, 336 ternary, 3 quaternary, and 2 quinary mixed systems. Almost all kinds of important physicochemical properties of ionic liquids mixtures were collected in this database. It covered 39 kinds of different physicochemical properties, such as crystallization temperature, density, viscosity, surface tension, conductivity, sound of speed, refractive index, phase equilibrium, isentropic compressibility, isothermal compressibility, expansibility, vapor pressure, thermodynamic functions of solution, etc.

In 2009, on the basis of database the physicochemical properties handbook of pure ionic liquids, entitled *Ionic Liquids: Physicochemical Properties*, was published by Elsevier. Herein, we planned a handbook of ionic liquid mixture. The handbook is divided into two parts. The first part mainly introduces the properties of ionic liquid mixtures, such as volumetric properties, transport properties, phase equilibria, etc., which includes the methods of measurements, fitting, and prediction. The second part contains nine chapters which are about physical and chemical properties data of ionic liquids mixtures; according to the classification of cations structure, the chapters respectively contain imidazolium, triazolium, pyrrolidinium, piperidinium, pyridinium, isoquinolinium, sulfonium, ammonium, and phosphonium. We hope that this handbook could provide useful references for scientific workers, promote the basic theoretical innovation of ionic liquids, and help push on the industrial application process of ionic liquids.

1.2 Properties of Ionic Liquid Mixtures

1.2.1 Volumetric Properties

The volumetric properties refer to be closely related with volume change of substance, such as density, molar volume, partial molar volume, excess molar volume, compressibility, expansibility, etc. The multicomponent mixtures containing ionic liquids are very complex systems, because they depend not only on molecular-molecular interaction but also on the ion–ion and ion–molecular interactions. Meanwhile, one of the factors affecting structural effects also has to be considered that arise from interstitial accommodation due to differences in molar volume and free volume between solution components. The knowledge of volumetric properties may help to test molecular simulation theories or models related to ionic liquids.

Furthermore, they will provide information and available data for the engineering design and optimization. So, the volumetric properties are basic and important thermodynamic properties.

The density is one of the volumetric properties, and major properties are calculated based on them; therefore, the reports and investigations about density are many more, including mixtures of organic solvents and ionic liquids, gases and ionic liquids, solid and ionic liquids, etc. In a general way, the measurement densities of ionic liquids mixtures depend on temperature, pressure, and component. Densities of ionic liquid mixtures at different temperatures for the whole range of composition can be correlated by using the linear equation or second-order polynomial.

$$\rho = \sum_{i=0}^{n} A_i T^i \tag{1.1}$$

where ρ is the density of mixtures, A is coefficients of equation, T is the temperature, $n = 1$ or 2.

Usually, the densities are fitted with composition of mixture containing ionic liquid distinctly nonlinear; this phenomenon is different from general organic solvent mixtures. Geppert-Rybczyńska et al. [1] applied the Connors and Wright equation [2] that is used for correlating concentration dependencies of surface tensions to describe the change of density with composition, and the correlation is satisfactory.

$$\rho = \rho_1 - \left[1 + \frac{bx_1}{(1 - ax_1)}\right](1 - x_1)(\rho_1 - \rho_2) \tag{1.2}$$

where ρ_1 and ρ_2 are densities of pure compounds, x_i is the mole fraction of component i of the mixture, a and b are fitting constants.

The molar volume (V_{m}) and the excess molar volume ($V_{\mathrm{m}}^{\mathrm{E}}$) can be calculated from above measuring densities data of mixtures. The molar volume is defined as follows:

$$V_{\mathrm{m}} = \frac{x_1 M_1^o + x_2 M_2^o}{\rho} \tag{1.3}$$

where M_i^o is the molar mass of the pure component i, x_i is the mole fraction of component i of the mixture.

The excess molar volume can be calculated according to the following equation:

$$V_{\mathrm{m}}^{\mathrm{E}} = V_{\mathrm{m}} - \sum_{i=1}^{2} x_i V_{\mathrm{m},i} \tag{1.4}$$

where $V_{\mathrm{m},i}$ is the molar volume of component i of the mixture. The values of $V_{\mathrm{m}}^{\mathrm{E}}$ can be fitted by Redlich–Kister type polynomial equation: [3–5]

$$V_{\mathrm{m}}^{\mathrm{E}} = x(1-x)\sum_{i=0}^{n} A_i (2x-1)^i \tag{1.5}$$

where x is the mole fraction of the one component of mixture, A_i are the adjustable parameters, and n is the order of polynomial equation, normally, $n = 4$ or 5.

In most cases, the V^{E} are all negative and asymmetric over the entire composition range, only V^{E} of a few ionic liquid mixtures are all positive or both negative and positive. The value of V^{E} is affected by the intermolecular interaction forces between the components of the mixtures and the differences in size and shape of molecules.

Further, the partial molar volumes $\overline{V}_1$ and $\overline{V}_2$ can be evaluated using the following equations:

$$\overline{V}_1 = V_{\mathrm{m}}^{\mathrm{E}} + V_{\mathrm{m},1} + (1-x)\left(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial x\right)_{p.T} \tag{1.6}$$

$$\overline{V}_2 = V_{\mathrm{m}}^{\mathrm{E}} + V_{\mathrm{m},2} + x\left(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial x\right)_{p.T} \tag{1.7}$$

Differentiation of Eq. 1.5 with respect to x_1 and combination of the results of differentiation with Eqs. 1.6 and 1.7 leads to the following equations for the partial molar volumes:

$$\overline{V}_1 = V_{\mathrm{m},1} + (1-x)^2\sum_{i=0}^{n} A_i (1-2x)^i + 2x(1-x)^2\sum_{i=0}^{n} A_i (t)(1-2x)^{i-1} \tag{1.8}$$

$$\overline{V}_2 = V_{\mathrm{m},2} + x^2\sum_{i=0}^{n} A_i (1-2x)^i + 2x^2(1-x)\sum_{i=0}^{n} A_i (t)(1-2x)^{i-1} \tag{1.9}$$

The partial molar volume at infinite dilution provides information about solute–solvent interactions that are independent of the composition. It is obtained from the following equations:

$$\overline{V}_1{}^{\infty} = V_{\mathrm{m},1} + \sum_{i=0}^{n} A_i \tag{1.10}$$

$$\overline{V}_2{}^{\infty} = V_{\mathrm{m},2} + \sum_{i=0}^{n} A_i (-1)^i \tag{1.11}$$

So, from Eqs. 1.10 and 1.11, the partial excess molar volumes at infinite dilution can be calculated:

$$\overline{V_1{}^{\mathrm{E}}}^{\infty} = \sum_{i=0}^{n} A_i \tag{1.12}$$

$$\overline{V_2{}^{\mathrm{E}}}^{\infty} = \sum_{i=0}^{n} A_i (-1)^i \tag{1.13}$$

Matkowska D. et al. [6] take into account the effect of both composition and temperature on the density, and the densities of mixtures can be expressed by the Eq. 1.14. So, the excess molar volumes are calculated from Eq. 1.15.

$$\rho(T,x_1) = \frac{M_1x_1 + M_2x_2}{\frac{M_1x_1}{\rho_1^0(T)} + \frac{M_2x_2}{\rho_2^0(T)} + V^{\mathrm{E}}(T,x_1)} \tag{1.14}$$

$$V^E = M_1x_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + M_2x_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \tag{1.15}$$

where M_1 and M_2 are molecular weights of the pure components and ρ, ρ_1, and ρ_2 are densities of the mixture and the pure components, respectively.

Because densities of pure compounds considering pressure were correlated by the Tait equation in the form [7]

$$\rho(T,p) = \frac{\rho_0(T,p_0)}{1 - Aln\frac{B(T)+p}{B(T)+p_0}} \tag{1.16}$$

where the reference pressure $p_0 = 0.1$ MPa, the $\rho(T)$ and $B(T)$ have the following functions of temperature

$$\rho_0(T,p_0) = \rho_{00} + \rho_{01}(T/K) + \rho_{02}(T/K)^2 + \rho_{03}(T/K)^3 \tag{1.17}$$

$$B(T) = B_0 + B_1(T/K) + B_2(T/K)^2 \tag{1.18}$$

So, the densities of the mixture were correlated by the following twelve-parameter equation in which the excess volume was formally represented by a sum of van Laar terms in which two such terms turned out to be suitable.

$$\rho(T,p,x_1) = \frac{M_1x_1 + M_2x_2}{\frac{M_1x_1}{\rho_1(T,p)} + \frac{M_2x_2}{\rho_2(T,p)} + x_1x_2\left(\frac{a_0(T,p)}{b_0(T,p)x_1 + x_2} + \frac{a_1(T,p)}{b_1(T,p)x_1 + x_2}\right)} \tag{1.19}$$

Correspondingly, the excess molar volumes are reproduced by the equation

$$V^{\mathrm{E}}(\mathrm{T},p,x_1) = x_1x_2\left(\frac{a_0(T,p)}{b_0(T,p)x_1 + x_2} + \frac{a_1(T,p)}{b_1(T,p)x_1 + x_2}\right) \tag{1.20}$$

where the $a_i(T, p)$ and $b_i(T, p)$ coefficients depend linearly on T and p.

The apparent molar volumes, $V_{\phi 1}$ and $V_{\phi 2}$ can be calculated with the equations:

$$V_{\phi 1} = \left[V_m - (1 - x)V_{m,2}\right]/x \tag{1.21}$$

$$V_{\phi 2} = \left[V_m - xV_{m,1}\right]/(1 - x) \tag{1.22}$$

Combining Eq. 1.4, $V_{\phi 1}$ and $V_{\phi 2}$ can be expressed as:

$$V_{\phi 1} = V_{\mathrm{m},1} - V_{\mathrm{m}}^{\mathrm{E}}/x \tag{1.23}$$

$$V_{\phi 2} = V_{\mathrm{m},2} - V_{\mathrm{m}}^{\mathrm{E}}/(1 - x) \tag{1.24}$$

The isobaric thermal expansivity (α_p) can be calculated on the basis of the volumetric data:

$$\alpha_p = \frac{1}{V_\mathrm{m}}\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{1.25}$$

The excess thermal expansion coefficient α_p^E is defined as follows:

$$\alpha_p^{\mathrm{E}} = \alpha_p - \left(\phi_1 \alpha_{p,1} + \phi_2 \alpha_{p,2}\right) \tag{1.26}$$

where $\alpha_{p,i}$ are the thermal expansion coefficients for pure components i, ϕ_i are the volume fractions for pure components i, defined as:

$$\phi_i = \frac{x_i V_{\mathrm{m},i}}{\sum_{i=1}^{2} x_i V_{\mathrm{m},i}} \tag{1.27}$$

The limiting apparent expansivity ϕ_E^0 could be estimated using the following relation:

$$\phi_E^0 = \partial V_\phi^0 / \partial T \tag{1.28}$$

where V_ϕ^0 is the limiting values of apparent molar volume (equal to the partial molar volume at infinite dilution).

Isentropic compressibility k_S is defined as

$$k_\mathrm{S} = -\frac{1}{V_\mathrm{m}}\left(\frac{\partial V_\mathrm{m}}{\partial p}\right)_S = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_S \tag{1.29}$$

and is also given by the Newton−Laplace equation

$$k_\mathrm{S} = \frac{1}{\rho u^2} = \frac{V_\mathrm{m}}{M_\mathrm{m} u^2} \tag{1.30}$$

where M_m and u are the molar mass and speed of sound of the mixture, respectively. Molar isentropic compression $k_{S,m}$ is defined from the isentropic compressibility as

$$k_{\mathrm{S,m}} = -\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_S = V_{\mathrm{m}} k_{\mathrm{S}} = \frac{V_{\mathrm{m}}^2}{M_{\mathrm{m}} u^2} \tag{1.31}$$

Apparent molar adiabatic compressibility k_ϕ can be calculated from the following equation:

$$k_\phi = \frac{M k_{\mathrm{S}}}{\rho} - \frac{1000\left(k_{\mathrm{S,0}}\rho - k_S \rho_0\right)}{m \rho \rho_0} \tag{1.32}$$

where M is the molar mass of the solute, m is the molality, ρ_0 and $k_{\mathrm{S,0}}$ are the densities and isentropic compressibility of solvent.

Industrial applications often require specific data to support the design process, but it makes harder to obtain accurate experimental data at some harsh conditions in the applications; at this time, the models predict seem essential based on a large amounts of existing experimental data. Therefore, many researchers focus on the study of models that could predict the volumetric properties of ionic liquid mixtures.

The models that predict the densities of mixtures are mostly semi-theoretical equation of state (EOS). Hosseini et al. [8] used a simple equation to predict the volumetric properties of binary mixtures including an ionic liquid, the equation is proposed by Spencer and Danner [9], and the mixing rule is developed by Li, Spencer, and Danner [10]. The corresponding equations are as follows:

$$\rho_{mix.} = \left(\sum_i \frac{P_{Ci}}{R_{xi} T_{Ci}}\right)^{Z_{RA\ mix.}^{-\left(1+\tau_{mix.}^{2/7}\right)}} \tag{1.33}$$

where:

$$Z_{RA\ mix.} = \sum_i x_i Z_{RAi} \tag{1.34}$$

and

$$\tau_{mix.} = 1 - (T/T_{C\ mix.}) \tag{1.35}$$

the mixing rule for the reduced temperature is expressed as:

$$T_{C\ mix.} = \sum_i x_i T_{Ci} \tag{1.36}$$

Yousefi [11] applied Tao and Mason equation of state (TM EOS) [12] based on statistical–mechanical perturbation theory to binary mixtures of ionic liquids. The equations are expressed as follows:

$$\frac{P}{\rho KT} = 1 + (B - a)\mathrm{\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} + A_1(\alpha - B)\mathrm{b}\rho^2 \frac{\left(e\dfrac{kT_c}{T} - A_2\right)}{1 + 1.8(b\rho)^4} \tag{1.37}$$

where

$$A_1 = 0.143 \tag{1.38}$$

$$A_2 = 1.64 + 2.65\left[e^{(k-1.093)} - 1\right] \tag{1.39}$$

$$k = 1.093 + 0.26\left[(\omega + 0.002)^{\frac{1}{2}} + 4.50(\omega + 0.002)\right] \tag{1.40}$$

where ω is the Pitzer acentric factor, λ is an adjustable parameter, ρ is the number density, T_c is the critical temperature, kT has usual meaning, B is the second virial coefficient, α is the scaling parameter, and b is the effective van der Waals covolume.

Hosseini et al. [13–15] developed a perturbed hard-sphere equation of state (PHS EOS) for predicting the densities of several ionic liquids and their mixtures. The general frame of the PHS EOS for ionic liquids mixtures has the form:

$$\frac{P}{\rho kT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{\rho}{kT}\sum_i^m\sum_j^m x_i x_j a(T)_{ij} \tag{1.41}$$

where x_i and x_j are the mole fractions of the ith and jth components, respectively. η is the packing fraction of mixtures of hard sphere [16]. This parameter is defined by the following expression:

$$\eta = \frac{\rho}{4}\sum_i^m x_i b(T)_i \tag{1.42}$$

As for binary mixtures, the hard-sphere covolumes, $b(T)_{ij}$ are additive according to following expression:

$$b(T)_{ij} = 1/8\left[b(T)_i^{\;1/3} + b(T)_j^{\;1/3}\right]^3 \tag{1.43}$$

The attractive forces between two hard-sphere species of mixtures including i and j components can be written as follows:

$$a(T)_{ij} = \frac{2\pi}{3(\rho^*)_{ij}} kT^*(F_a)_{ij} \tag{1.44}$$

Hosseini et al. [17] applied the following combining rules to T_{ref}, ρ^* and the universal function F_a:

$$\left(T_{ref}\right)_{ij} = \sqrt{T_{ref,i}T_{ref,j}} \tag{1.45}$$

$$\left(\rho_{ij}^{*}\right)^{-1/3} = \frac{1}{2}\left[\left(\rho_{i}^{*}\right)^{-\frac{1}{3}} + \left(\rho_{j}^{*}\right)^{-1/3}\right] \tag{1.46}$$

$$(F_a)_{ij} = \sqrt{(F_a)_{ii}(F_a)_{jj}} \tag{1.47}$$

In case of V_m^E, the Prigogine-Flory-Paterson (PFP) [18] and the Flory-Benson-Treszczanowicz (FBT) [19] models are common use prediction models. They are very useful in predicting and correlating the thermodynamic properties of binary mixtures of polar and nonpolar molecules.

1.2.2 Transport Properties

The transport properties of ionic liquids with molecular solvents that are commonly used for process analyses in industrial applications are the viscosity, the diffusion coefficient, the surface tension, the speed of sound, etc. Overall, there is still a lack of data on their transport properties because of the wide variety of ionic liquids.

1.2.2.1 Viscosity

Generally, ionic liquids are much more viscous than conventional organic solvents, which to some extend limit their range of industrial applications. However, the viscosity of ionic liquids is different from the density, in that it shows a remarkable influence of impurity: the presence of a trace of impurities can result in dramatic decreases in viscosity [20]. Therefore, the viscosity of ionic liquid mixtures is much smaller than pure ionic liquid.

The common measurements of the viscosity of ionic liquids are rolling sphere [21–23], falling body [24–28], and moving piston [29, 30]. Among them, the most commonly used method is falling body.

The viscosity of ionic liquids mixtures is related with temperature, the structure of ionic liquid, the size of solvent, the interaction between solute and solvent, and so on. Generally, the values of viscosity decrease with increasing temperature, which can be a result of the disruption of intramolecular hydrogen bonding between the ionic liquid molecules. As for the influence of ionic liquid structures and the solvent, the viscosities increase with increasing number of carbon atoms in the linear alkyl group in the cations of ionic liquid[31, 32]. Domańska et al. [33–35] found that the values of viscosities increase as the alkyl chain of alcohol solutions increases at the same temperature (see Fig. 1.1). The same result can be seen in ref [36]. Gómez et al. [37] measured the viscosities of water + 1-hexyl-3-methylimidazolium chloride and water + 1-octyl-3-methylimidazolium chloride; they found that the modification of viscosity deviations is related to interactions of the type water–ion and ion–ion.

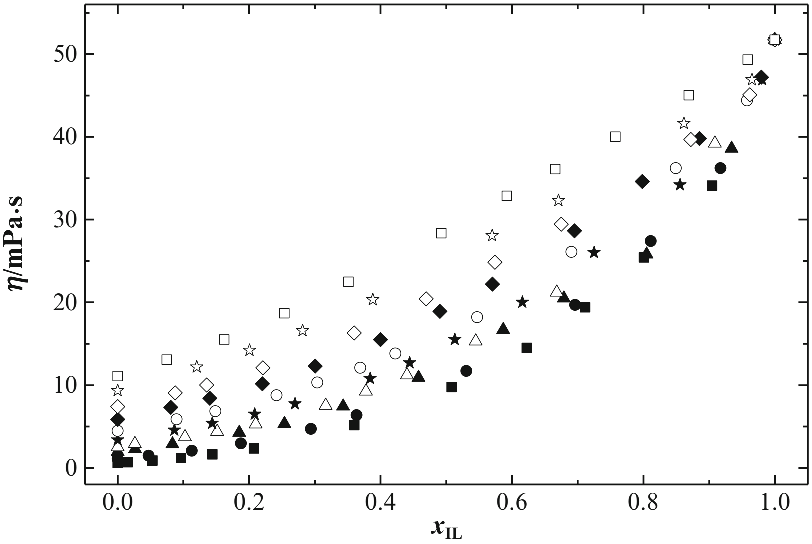

Fig. 1.1 The viscosities of ionic liquid alcohol solutions as a function of mole fractions of 1-butyl-3-methylimida-zolium thiocyanate ([BMIM][SCN], x_1) at $T = 298.15$ K. ■: [BMIM][SCN] + methanol, ●: [BMIM][SCN] + ethanol, ▲: [BMIM][SCN] + 1-propanol, △: [BMIM][SCN] + 1-butanol, ★: [BMIM][SCN] + 1-pentanol, ○: [BMIM][SCN] + 1-hexanol, ◆: [BMIM][SCN] + 1-heptanol, ◇: [BMIM][SCN] + 1-octanol, ☆: [BMIM][SCN] +1-nonanol, □: [BMIM][SCN] + 1-decanol

The relationship between viscosities of ionic liquid mixtures and temperature can be correlated by Vogel-Tammann-Fulcher (VTF) equation [38]:

$$\ln\eta = A + \frac{B}{T - T_0} \tag{1.48}$$

where η is the viscosities of mixtures, T is thermodynamic temperature, A, B, and T_0 are parameters.

In order to study solvent–solute interaction, the viscosity deviations ($\Delta\eta$) were calculated by the following relation:

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i\eta_i \tag{1.49}$$

where η and η_i are the viscosity of mixtures and pure components i, respectively.

As for binary mixtures, the values of $\Delta\eta$ can be fitted by Redlich-Kister-type polynomial equation: [3–5]

$$\Delta\eta = x_1x_2\sum_{i=0}^{n} A_i(1 - 2x_2)^i \tag{1.50}$$

where x_1 and x_2 are the mole fraction of the components 1 and 2, A_i are the adjustable parameters, and n is the order of polynomial equation. The optimum number of adjustable parameters was ascertained from an examination of the standard deviation (S):

$$S = \left[\frac{\sum \left(\Delta\eta_{\mathrm{exp}} - \Delta\eta_{\mathrm{cal}} \right)^2}{n} \right]^{1/2} \tag{1.51}$$

where n is the total number of experimental points, $\Delta\eta_{\mathrm{exp}}$ is the experimental value, and $\Delta\eta_{\mathrm{cal}}$ is the calculated value from Eq. 1.49.

So far, the related estimation methods of predicting the viscosities of ionic liquid mixtures are very scarce. Lashkarblooki et al. [39] used multilayer perceptron artificial neural network model to predict the viscosities of ternary mixtures containing ionic liquids. Their results indicated that this model is able to predict viscosity of ionic liquids ternary systems with a considerably high accuracy. Hu et al. [40] made the ionic liquid mixtures as electrolyte solutions and used a series of equations for prediction of the viscosity of mixed electrolyte solutions in predicting corresponding properties of mixed ionic liquid solutions. The results indicate that the method can provide good predictions for the multicomponent ionic liquid solutions.

1.2.2.2 Diffusion Coefficient

The diffusion coefficient (D) is a physical constant dependent on molecule size and other properties of the diffusing substance as well as on temperature and pressure. It is an important parameter to describe suitably diffusion mass transport phenomena [41, 42], and the diffusion coefficient of ionic liquids in some solvents can affect their use in separation processes [43] and catalytic reactions [44–46].

There are various methods available to measure diffusion coefficients of mixtures, such as impedance spectroscopy [47], polarization measurements,[47, 48] chronoamperometry [49, 50], diaphragm cell method [51], optical method [52], Taylor dispersion method [53, 54], and dynamic light scattering (DLS).[55–58] Among this methods, the Taylor dispersion method has been shown to be relatively fast, but it can be applied only in the regime of infinite dilution. DLS method is a suitable technique that is used in measuring mutual diffusivity coefficients of ionic liquids mixtures over a range of concentration [59, 60].

The diffusion coefficients of ionic liquid in solvents can be fitted to Arrhenius plots of the form:

$$D_{21} = D_0 exp\left(-\frac{E_a}{RT} \right) \tag{1.52}$$

where D_0 is a preexponential factor, E_a is the activation energy of the solute for diffusion. The subscript 1 and 2 represent ionic liquid and solvents, respectively.

The relationship between the diffusion coefficients of ionic liquid and the viscosities of solvents can be expressed by Stokes–Einstein equation:

$$D_{21} = \frac{k_{\mathrm{B}} T}{C\pi\eta_1 r_2} \tag{1.53}$$

where k_{B} is the Boltzmann constant, T is the temperature, the constant C is dependent on the boundary condition of the surface flow (four for the slip, six for the stick boundary condition), η_1 is the viscosity of the solvent, r_2 is the effective hydrodynamic radius of the solute.

The effect factors of self-diffusion coefficients and mutual diffusion coefficients are distinguished. So we discussed them separately.

The self-diffusion coefficients can be mainly influenced by size of ion, shape of ion, and magnitude of interaction between ions. For example, the self-diffusion coefficients of the ions in the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide decrease with increasing alkyl chain length[61]. Tokuda et al. [62] found that the sequence of self-diffusion coefficients of the ions in ionic liquids is 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([BMIM][TFSA]) > N-butylpyridinium bis(trifluoromethylsulfonyl)amide ([bpy][TFSA]) > N-butyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)amide ([btma][TFSA]) > N-butyl-N-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide ([bmpro][TFSA]), which can be seen that the shape of the cations could influence the self-diffusion coefficients of the ions. Tsuzuki et al. [63] calculated the stabilization energies of [EMIM][BF_4], [EMIM][CF_3SO_3], and [EMIM][TFSA] and found that the self-diffusion coefficients of the ions in [EMIM][TFSA] are larger than those in the other two ionic liquids, although the size of $TFSA^-$ is larger than other anions. This is because the self-diffusion coefficients depend on the magnitude of the interaction between the anion and cation.

The mutual diffusion coefficients can be mainly influenced by the temperature, the size of solute, the interaction between solute and solvent, and the viscosity of solute. The mutual diffusion coefficients increase with increasing temperature. Sarraute et al. [64] found that diffusion coefficients decrease, in water, acetonitrile, and methanol, with increasing alkyl side chain in the cation for the 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_nMIM][TFSA]) ionic liquids. They also found that for the ionic liquids based on the [BMIM] cation, the diffusivities sequence in water are [BMIM][TFSA] < [BMIM][BF_4] ~ [BMIM][PF_6] < [BMIM]Cl. This is because as for different size of anions, larger ionic liquids diffuse more slowly than the smaller ones. Rausch et al. [60] found that for the ionic liquids-ethanol systems, the mutual diffusion coefficients are distinctly lower than those obtained for the mixtures with acetone. This can be explained for: The formation of hydrogen bonds between ethanol and the ions retard the mutual diffusion process. They also found that the larger the viscosities of pure ionic liquids, the lower the mutual diffusivities in the solvent. This is because the increasing viscosity reduced the mobility of the molecules.

The diffusion coefficients of organic molecules can be estimated by the Wilke–Chang equation [65]:

$$D_{\mathrm{AB}}^{0} = \frac{a(\phi M_{\mathrm{B}})^{1/2}T}{\eta_{\mathrm{B}} V_{A}^{0.6}} \tag{1.54}$$

where D_{AB}^{0} is the diffusion coefficient of solute A (ionic liquid) in solvent B, a is a constant, ϕ is the association parameter for the solvent, M_{B}, η_{B} are molecular weight and viscosity of solvent, respectively, V_{A} is molar volume of solute.

The diffusion of ionic liquids in water could also be regarded as the diffusion of electrolyte, and the diffusion coefficients of electrolytes are related to infinite dilution conductance by the Nernst–Haskell equation [66]:

$$D_{\mathrm{AB}}^{0} = \frac{RT}{F^{2}} \frac{|z_{+}| + |z_{-}|}{|z_{+}z_{-}|} \frac{\Lambda_{+}^{0}\Lambda_{-}^{0}}{\Lambda_{+}^{0} + \Lambda_{-}^{0}} \tag{1.55}$$

where D_{AB}^{0} is the diffusion coefficient of ionic liquid in water at infinite dilution, R is the gas constant, T is the absolute temperature, F is the Faraday's constant, z_{+} and z_{-} are the charge numbers of cation and anion molecules, respectively, Λ_{+}^{0} and Λ_{-}^{0} are the infinite dilution conductances of the cation and anion molecules, respectively.

The self-diffusion coefficients of the ions at infinite dilution could also be evaluated using the Nernst expression [66]:

$$D_{\mathrm{ion}}^{0} = \frac{RT\Lambda_{\mathrm{ion}}^{0}}{|z_{\mathrm{ion}}|F^{2}} \tag{1.56}$$

where D_{ion}^{0} is the self-diffusion coefficient of ions at infinite dilution, R is the gas constant, T is the absolute temperature, $\Lambda_{\mathrm{ion}}^{0}$ is the infinite dilution molar conductance of the ion, and z_{ion} is the charge number of the ion.

1.2.2.3 Surface Tension

Surface tension refers to resistance properties of liquid substances on some force, and it is one of the most important properties of ionic liquids. The surface tension data is an important factor for engineers considered in chemical process and reactor engineering, biochemical engineering, electrical engineering, etc. [67].

The surface tension values of ionic liquids are mainly dependent upon the structure of cations and anions that are present at the surface of ionic liquids [68]. Wang et al. [69] measured surface tension of ionic liquids based on 1-C_nH_{2n+1}-3-methylimidazolium ([$C_n$mim]) with two kinds of fluorinated anions (BF_4^- and PF_6^-) ($n = 2-7$; $4-7$, respectively) by using a Wilhelmy plate apparatus. It can be seen that the surface tension of the same ionic liquid decreases linearly with a rise in temperature. The dependence could be described by the empirical Eötvös equation [70]:

$$\sigma = \frac{k(T_c - T)}{V_{\mathrm{M}}^{2/3}} \tag{1.57}$$

where k is an empirical constant, T_{C} is the critical temperature. V_{M} is the molecular volume of ionic liquids, respectively.

It also can be seen that the surface tension of the ionic liquids in the same anions decreases with the increase in alkyl chain length at a given temperature (see Table 1.1). This conclusion may be explained by Langmuir's principle of independent surface action [71]. As for the influence of anions, Xu et al. [68] found that the

Table 1.1 Values of the surface tension of the ionic liquids

Ionic liquids	$\sigma/(\mathrm{mJ}\cdot\mathrm{m}^{-2})$ at 298.15 K
$[C_2mim][BF_4]$	50.4
$[C_3mim][BF_4]$	48.6
$[C_4mim][BF_4]$	43.9
$[C_5mim][BF_4]$	40.8
$[C_6mim][BF_4]$	37.0
$[C_7mim][BF_4]$	36.1
$[C_4mim][PF_6]$	48.0
$[C_5mim][PF_6]$	43.0
$[C_6mim][PF_6]$	38.6
$[C_7mim][PF_6]$	35.7

surface tension of carboxylic acids decreases in the series $HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3(CH_2)_2COOH$.

There are some correlation methods for the prediction of the surface tension of ionic liquids. The common methods include parachors, corresponding state theory (CST), and group contribution methods.

The parachors method is based on an empirical equation (Eq. 1.58) proposed by MacLeod [72]:

$$\sigma^{\frac{1}{4}} = K\rho \tag{1.58}$$

where K is a temperature independent constant characteristic of the compound.

Sugden [25] proposed a modification and defined parachor (P_{ch}).

$$P_{ch} = KM_{\mathrm{w}} = M_{\mathrm{w}}\sigma^{\frac{1}{4}}/\rho \tag{1.59}$$

where M_{w} is the molecular weight.

Deetlefs et al. [73] were the first to employ the parachor for prediction of the surface tension of ionic liquids, and the parachors were calculated using group contribution method by Knotts et al. [74]. Then, Gardas and Coutinho [75] proposed another correlation for the surface tension of ionic liquids based on the molecular volume of the ion pair:

$$\sigma = {}^{d}\Big/_{V^{2/3}} \tag{1.60}$$

where V is the molecular volume in Å^3, and $d = 2147.761 \pm 18.277(\mathrm{mN}\cdot\mathrm{m}^{-1})$ Å^2.

Although these two models could provide a good estimation of the surface tension of ionic liquids, they can be used just for imidazolium-based ionic liquids.

Recently, Mousazadeh and Faramarzi [76] proposed the corresponding states theory (CST) correlation for the surface tension of ionic liquids. They used the melting and boiling points of ionic liquids instead of critical properties:

$$\sigma = 0.819\left(\frac{T_{\mathrm{b}} - T}{T_{\mathrm{b}} - T_{\mathrm{m}}}\right)\sigma_m + 0.500\left(\frac{T}{T_{\mathrm{b}}}\right)\sigma_{\mathrm{m}} \tag{1.61}$$

where σ_{m} is the surface tension at melting temperature T_{m}, and T_{b} is the boiling temperature.

The drawback of the model is its lack of predictive power although it revealed a small average absolute relative deviation (AARD). On the other hand, many ionic liquids do not have a melting point, and that the boiling temperatures of the ionic liquids are as elusive as their critical temperatures, which limit its application to a certain extent.

Gharagheizi et al. [77] used the group contribution method to estimate surface tension of ionic liquids. Their method includes 12 substructures related to chemical structure of anion, 7 substructures related to the chemical structure of cation and temperature (see Eq. 1.62).

$$\sigma = \sum_{i=1}^{N_a} N_{ai}\sigma_{ai} + \sum_{i=1}^{N_c} N_{ci}\sigma_{ci} + A + BT \tag{1.62}$$

where N_{ai}, N_{ci}, σ_{ai}, σ_{ci}, A, B, N_a, N_c are the number of occurrence of ith substructure of anions and cations, the contribution of the ith substructure of anions and cations, the intercept of Eq. 1.62, the temperature coefficient, and the number of total substructures of anions and cations.

This method shows an AARD of 3.6 % from experimental data and can be used to predict the surface tension of various ionic liquids.

Wu et al. [78] proposed a corresponding-states group contribution method to estimate the surface tension of ionic liquids and developed a new equation based on the method:

$$\sigma = \sum_{i=0}^{3} a_i \left(\sum_{j=1}^{k} n_j \Delta\sigma_{0,j}\right)^i (1 - T_r)^{11/9} \tag{1.63}$$

where n_j is the number of groups of type j, and k is the total number of different groups in the molecular. The parameters a_i and $\Delta\sigma_{0,j}$ were estimated by minimizing the objective function O.F. in Eq. 1.64:

$$\text{O.F.} = \sum_{i=1}^{N_{\mathrm{P}}} \left[\left(\sigma_{\mathrm{calc}} - \sigma_{\exp}\right)^2\right]_i \tag{1.64}$$

where N_{P} represents the number of data points.

This method offers a simple approach for estimating surface tension of new ionic liquids and has a good accuracy.

So far, experimental data for surface tension of ionic liquids mixtures is very scarce. Domańska et al. [79] measured the surface tension of binary mixtures of several ionic liquids combined with different alcohols at different temperatures. It is found that surface tension values of mixtures increase with ionic liquids mole fraction increase. But as for the same ionic liquid, the increase of surface tension in different solvents presents different trends. For example, surface tension values of ([MMIM][CH_3SO_4] + methanol) mixtures showed a liner increase with the ionic liquid mole fraction increase, which indicates that the methanol molecules have strongly joined on the surface of ionic liquids. However, surface tension values of ([MMIM][CH_3SO_4] + ethanol/1-butanol) mixtures occurred at a breakpoint, and the values increase slowly before the breakpoint, whereas it increase sharply after breakpoint. It has also been found that the values of breakpoint are different for different ionic liquids mixtures. This may be caused by anionic and cationic hydrophobic nature or the hydrophobic nature of alcohols.

The surface tension of the ionic liquids aqueous solutions shows a different tendency compared to (ionic liquids + alcohols) mixtures. Rilo et al. [80] measured the surface tension of 1-alkyl-3-methylimidazolium tetrafluoroborate ([C_nMIM][BF_4], $n = 2,4,6$) aqueous solutions. Since surface tension values of these ionic liquids are smaller than surface tension values of water, the surface tension decreases with the increasing of the ionic liquids mole fraction. Moreover, it was found that the surface tension decreases when the length of the alkyl chain increases over the whole composition. Jiang et al. [81] measured the surface tension of 1-butyl-3-methyl-imidazolium L-lactate + water mixtures. It was observed that at low mole fraction of ionic liquids (x_{IL}), the surface tension decreases sharply, and then decreases slowly while $x_{IL} > 0.1$. This indicates 1-butyl-3-methyl-imidazolium L-lactate acts as a surface active agent in aqueous solution.

The tendency of temperature effects on the surface tension of ionic liquid mixtures is the same as the pure ionic liquid. The surface tension measured at a given composition decreases with increasing temperature. The reason is that the surface tension drop caused by the molecular solvent becomes less significant at higher temperatures [82]. However, the temperature effect on the surface tension of ionic liquid mixtures is quite diverse, although the general trend of surface tension with temperatures is consistent [83]. (For example, for ([C_8mim][PF_6] + water) mixtures, the dependency of the surface tension with temperature is almost equal to that of the pure ionic liquid while for the [C_6mim][TFSA] + 1-octene) mixtures, the surface tension dependence on temperature is less significant than the pure ionic liquid).

Surface tension deviations of binary mixtures are obtained by Eq. 1.65:

$$\delta\sigma = \sigma - \sum_{i=1}^{2} x_i \sigma_i \qquad (1.65)$$

where σ and σ_i are the surface tension of mixture and component i, respectively; x_i is the mole fraction of component i.

1.2.2.4 Speed of Sound

The speed of sound (u) is a useful property, since it can derive many thermophysical properties including isentropic and isothermal compressibilities, isobaric thermal expansion coefficient, thermal pressure coefficient, the Joule–Thomson coefficient, isobaric and isochoric heat capacities, ratio of isobaric and isochoric heat capacities, and the reduced bulk modulus along with other properties [84].

The isentropic compressibility (K_s) was evaluated for the investigated systems from Laplace–Newton's equation

$$K_{\mathrm{s}} = \frac{1}{\rho u^2} \tag{1.66}$$

where u and ρ are speed of sound and density of the solution, respectively.

The isothermal compressibility $\left(K_T\right)$ could be calculated from the speed of sound [85]:

$$K_{\mathrm{T}} = \frac{1}{\rho}\left(\frac{1}{U^2} + \frac{T a_{\mathrm{P}}^2 M}{C_{\mathrm{P,m}}^0}\right) \tag{1.67}$$

where ρ is the density ($\mathrm{kg} \cdot \mathrm{m}^{-3}$), M is the molar mass ($\mathrm{kg} \cdot \mathrm{mol}^{-1}$), $a_{\mathrm{P}}$is the thermal expansion coefficient (K^{-1}), $C_{\mathrm{P,m}}^0$ is isobaric heat capacity ($\mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}$).

We can also obtain p-ρ-T data from the experimental speed of sound since it can be measured accurately at some pressures and it is a key quantity in the equation of state formulation. Dzida et al. [86] calculated the densities of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][TFSA]) under high pressures from speed of sound. Equations are as follows:

$$\left(\frac{\partial \rho}{\partial T}\right)_T = \frac{1}{u^2} + \frac{T\alpha^2}{C_{\mathrm{P}}} \tag{1.68}$$

$$\Delta\rho = \int_{P_1}^{P_2} \left(\frac{1}{u^2} + \frac{T\alpha^2}{C_{\mathrm{P}}}\right) dP \approx \int_{P_1}^{P_2} \frac{1}{u^2} dP + \frac{T\alpha^2}{C_{\mathrm{P}}} \Delta P \tag{1.69}$$

where $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ is the thermal expansion coefficient, C_{P} is the specific isobaric heat capacity. To calculate the density at P_2, ρ, α, and C_{P} at P_1 should be known, in addition to the speed of sound as a function of pressure.

The calculated data is in a good agreement with the experimental data reported in the literature.

The temperature dependence of speed of sound was correlated by means of a polynomial type equation:

$$u = \sum_{i=0}^{2} b_i T^i \tag{1.70}$$

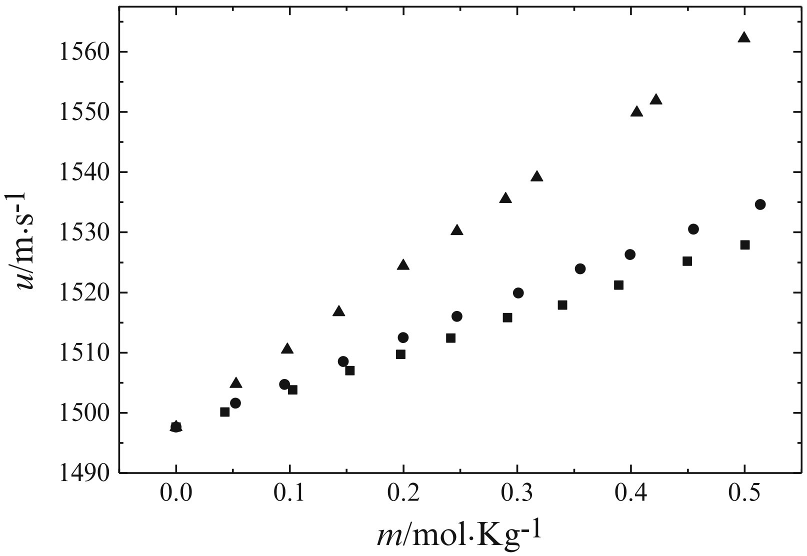

Fig. 1.2 The speed of sound as a function of molality of ionic liquids (m) at $T = 298.15$ K. ■: [Im]Cl; ●: [Mim]Cl; ▲: [Bmim]Cl

The speed of sound, u in m/s units can be estimated using the theoretical Auerbach's relation [87]:

$$u = \left(\frac{\sigma}{6.33 \times 10^{-10} \times \rho}\right)^{2/3} \tag{1.71}$$

where σ and ρ are the surface tension in $\mathrm{N \cdot m^{-1}}$ units and density in $\mathrm{kg \cdot m^{-3}}$ units, respectively. Gardas et al. [84] used this empirical relation to estimate the speeds of sound of imidazolium-based ionic liquids and found that this method had a better accuracy.

As for ionic liquids mixtures, their speed of sound could be influenced by temperatures, the structures of ionic liquid, the interaction between solute and solvent, and so on. Generally, the values of speed of sound decrease as temperature increases. Gardas et al. [88] measured the speed of sound of aqueous solutions of imidazolium chloride ([Im]Cl), 1-methyl imidazolium chloride ([Mim]Cl), and 1-butyl-3-methyl imidazolium chloride ([Bmim]Cl) in the concentration range of $0.05\ \mathrm{mol \cdot Kg^{-1}}$ to $0.5\ \mathrm{mol \cdot Kg^{-1}}$ at 298.15 K. From Fig. 1.2, we can see that the speed of sound increases with increasing of alkyl substituents on the imidazolium cation. The sequence is [Bmim]Cl > [Mim]Cl > [Im]Cl. Govinda et al. [89] measured the speed of sound of trimethylammonium acetate $[(CH_3)_3NH][CH_3COO]$ (TMAA), trimethylammonium hydrogen sulfate $[(CH_3)_3NH][HSO_4]$ (TMAS), and trimethylammonium dihydrogen phosphate $[(CH_3)_3NH][H_2PO_4]$ (TMAP) in dimethylsulfoxide (DMSO) over the whole concentration range at a wide range of

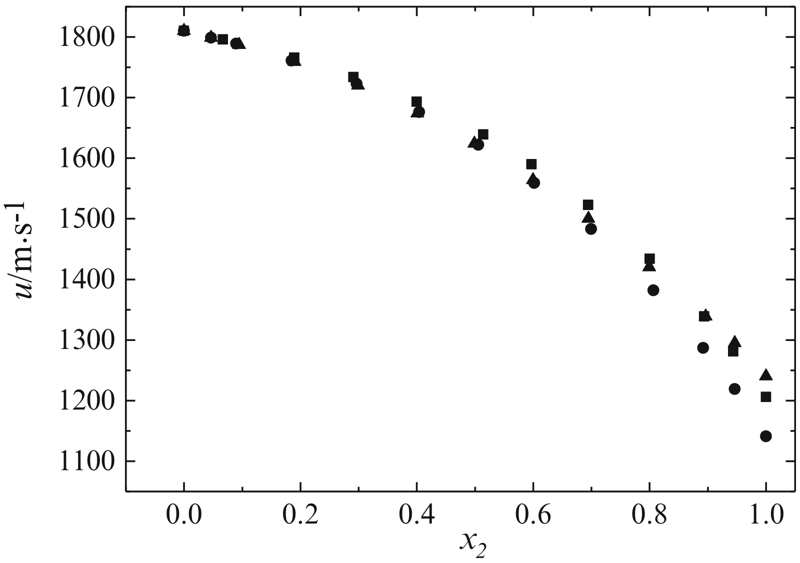

Fig. 1.3 The speed of sound as a function of mole fraction of ionic liquids (x_1) at $T = 298.15$ K. ■: 1-Propanol (1) + [BMpyr][dca] (2); ●: 2-Propanol (1) + [BMpyr][dca] (2); ▲: 1-Butanol (1) + [BMpyr][dca] (2)

temperatures. They found that the larger the anion size of ionic liquid, the higher the value of speed of sound. The sequence is TMAP > TMAS > TMAA. González et al. [90] found that the speed of sound of 1-butyl-1-methylpyrrolidinium dicyanamide ([BMpyr][dca]) mixtures is related to the interaction between [BMpyr][dca] and alcohol solvents (see Fig. 1.3).

1.2.3 Refractive Index

Refractive index (n_D) is a dimensionless number that describes how light, or any other radiation, propagates through that medium. It is one of the most important physical properties of transparent solid, liquid, and gas, and it can be determined accurately and conveniently. As a standard of purity of liquid, it is more reliable than the boiling point. In general, it is influenced by concentration, temperature, wavelength, and pressure. Now it is usually used in designing of laser systems, monitoring of environment pollution, and measuring material homogeneity of solidified transparent materials [91].

To better understand the nature of ionic liquids and expand their applications, detailed knowledge on the physical properties of ionic liquids and ionic liquids mixtures, such as refractive index, is required [92]. So, currently, much refractive index data of ionic liquids and ionic liquids mixtures is determined to understand their thermodynamic behavior.

Seki et al. [93] studied the relationship between refractive index of ionic liquid and the molecular polarizability of ion pair by measuring 17 types of room temperature ionic liquids at various temperatures. The result is that the refractive index of ionic liquids increase as the polarizability increases and shows a good linear tendency. The ionic liquids can be designed with high refractive indexes by using the above conclusion.

Generally, as for ionic liquids mixtures, it can be seen that the refractive index of the mixtures increases with the increase of the mole fraction of ionic liquids, and it decreases with the increase of temperature [94]. Iglesias-Otero et al. [95] found that the refractive index of [Bmim][BF_4] systems data can be fit well with the expression:

$$n_D = \frac{C_1 + C_2 x}{1 + C_3 x} \tag{1.72}$$

where x is the molar fraction of [Bmim][BF_4], C_i are parameters.

Shekaari et al. [96] measured the refractive index of 1-Pentyl-3-methylimidazolium Chloride ([PnMIm]Cl) aqueous solutions and found that the refractive index of the mixtures can be fitted with a polynomial expansion of the form:

$$n_D - n_D^* = \sum_{i=1}^{3} A_i m^i \tag{1.73}$$

where m is the molality of the ionic liquid, n_D^* is the refractive index of pure water, and A_i are fitting parameters.

To date, the estimation methods for the refractive index of room temperature ionic liquids are very few. Rilo et al. [97] proposed a very simple model (Eq. 1.74) to reproduce the refractive index of an ionic liquid mixture.

$$n_D = \left(\varnothing_{IL} n_{IL}^2 + \varnothing_S n_S^2\right)^{1/2} \tag{1.74}$$

where $\varnothing_{IL}$ and $\varnothing_S$ are the volume fraction of ionic liquid and solvent, respectively. And that they can be calculated by Eqs. 1.75 and 1.76:

$$\varnothing_{IL} = \frac{x_{IL} M_{IL} \rho_S}{x_{IL} M_{IL} \rho_S + x_S M_S \rho_{IL}} \tag{1.75}$$

$$\varnothing_S = \frac{x_S M_S \rho_{IL}}{x_{IL} M_{IL} \rho_S + x_S M_S \rho_{IL}} \tag{1.76}$$

where $x_{IL}$and x_S are the molar fraction of ionic liquid and solvent, M_{IL} and M_S are the molar mass of ionic liquid and solvent, and ρ_{IL} and ρ_S are the density of ionic liquid and solvent, respectively.

The model is very convenient, and as long as we know the real density for all compositions, the refractive index could be estimated accurately.

Kurnia et al. [98] predicted the refractive index of ionic liquids mixtures by using the following expressions proposed by Lorentz–Lorenz (Eq. 1.77), Dale–Gladstone (Eq. 1.78), and Eykman (Eq. 1.79) [99–101]:

$$\frac{n_{\mathrm{Dm,\,calc.}}^2 - 1}{n_{\mathrm{Dm,\,calc.}}^2 + 2} = \sum_{i=1}^{N}\left[\varphi_i\left(\frac{n_{\mathrm{Di}}^2 - 1}{n_{\mathrm{Di}}^2 + 2}\right)\right] \tag{1.77}$$

$$n_{\mathrm{Dm,\,calc.}} - 1 = \sum_{i=1}^{N}[\varphi_1(n_{\mathrm{Di}} - 1)] \tag{1.78}$$

$$\frac{n_{\mathrm{Dm,\,calc.}}^2 - 1}{n_{\mathrm{Dm,\,calc.}}^2 + 0.4} = \sum_{i=1}^{N}\left[\varphi_i\left(\frac{n_i^2 - 1}{n_i^2 + 0.4}\right)\right] \tag{1.79}$$

where $n_{\mathrm{Dm,calc.}}$ is the refractive index of the mixture, and $n_{\mathrm{D}i}$and φ_i are the refractive index and the volumetric fraction of components i, respectively.

This method shows a small deviation when compared with the experimental refractive index data for all the four binary mixtures.

There are different ways of defining the deviations in the refractive index (Δn_{D}). The earlier one is defined as the following equation [102] like any other deviation of a physical property of a liquid mixture. And it is the most commonly used equation.

$$\Delta n_{\mathrm{D}} = n_{\mathrm{D}} - \left(x_1 n_{\mathrm{D},\,1} + x_2 n_{\mathrm{D},\,2}\right) \tag{1.80}$$

where x_i is the mole fraction, and the subscripts 1 and 2 represent pure component 1 and component 2.

This is a convenient means of reporting high-quality data but is not physically significant, so some new expressions were proposed.

Brocos et al. [103] defined the deviations in the refractive index as the following equation:

$$\Delta n_{\mathrm{D}} = n_{\mathrm{D}} - \left(\varnothing_1 n_{\mathrm{D},\,1} + \varnothing_2 n_{\mathrm{D},\,2}\right) \tag{1.81}$$

where $\varnothing$ is the volume fraction, and the subscripts 1 and 2 represent pure component 1 and component 2.

Iglesias-Otero et al. [104] proposed a more rigorous definition of the deviations in the refractive index, and the equation is as follows:

$$\Delta n_{\mathrm{D}} = n_{\mathrm{D}} - \left[\frac{\left(n_{\mathrm{D},\,1}\right)^2\left(n_{\mathrm{D},\,2}\right)^2 + 2\varnothing_1\left(n_{\mathrm{D},\,1}\right)^2 + 2\varnothing_2\left(n_{\mathrm{D},\,2}\right)^2}{2 + \varnothing_1\left(n_{\mathrm{D},\,2}\right)^2 + \varnothing_2\left(n_{\mathrm{D},\,1}\right)^2}\right]^{½} \tag{1.82}$$

where $\varnothing$ is the volume fraction, and the subscripts 1 and 2 represent pure component 1 and component 2.

Reis et al. [105] defined the deviations in the refractive index as the following equation:

$$\Delta n_{\mathrm{D}} = n_{\mathrm{D}} - \left[\varnothing_1\left(n_{\mathrm{D},1}\right)^2 + \varnothing_2\left(n_{\mathrm{D},2}\right)^2\right]^{1/2} \tag{1.83}$$

where $\varnothing$ is the volume fraction, and the subscripts 1 and 2 represent pure component 1 and component 2.

The values of Δn_{D} that calculated by any above equations could be correlated with the ionic liquid mole fraction (x_1) or volume fraction ($\varnothing_1$) by the Redlich-Kister [106] equation.

The values of Δn_{D} are influenced by the structures of ionic liquids and solvents. Vercher et al. [94] found that that Δn_{D} decreases with increasing the length of alkyl chains of imidazolium ionic liquids. The deviations in the refractive index follow the sequence [emim][triflate] (1-ethyl-3-methylimidazolium trifluoromethanesulfonate) > [bmim][triflate] (3-butyl-1-methylimidazolium trifluoromethanesulfonate) > [beim][triflate] (3-butyl-1-ethylimidazolium trifluoromethanesulfonate). This is caused by the volume expansion of the substituents. González et al. [107] found that the refractive index deviation decreases as the length of the chain of alcohol increases. They also found that the refractive index deviation of the OH group that is in the secondary position on the chain of alcohol is higher than its OH group that is in the last position on the chain of alcohol. Namely, the sequence is methanol > 2-propanol > 1-propanol. The same behavior for mixtures of ionic liquids with alkanols can be seen from reports by Arce et al. [108] and Vercher et al. [102] .

Iglesias-Otero et al. [104] found that the positive values of the deviations in the refractive index corresponded to negative excess volume values, and the peaks appeared almost at the same molar fraction for ionic liquids mixtures. The reason is that if the value of excess volume is positive, there is more free volume in the solution. So, as a result, its refractive index will be lower than in an ideal solution.

The molar refraction R of ionic liquids mixtures is very important, and it is a measure of the ability of molecular orbitals to be deformed under an electric field [103]. The molar refraction R is defined as the following equation [109]:

$$R = V_{\mathrm{m}}\left(n_{\mathrm{D}}^2 - 1\right)/\left(n_{\mathrm{D}}^2 + 2\right) \tag{1.84}$$

where V_{m} is molar volume.

1.2.4 Vapor–Liquid Equilibrium (VLE)

Vapor–liquid equilibrium (VLE) behavior data are very important for the design and development of the gas absorption and separation, distillation process, etc. Ionic liquids are usually used as absorbents or entrainers since they have the advantage of high separation factors, easy operation, and no entrainment in the top product of the column for the distillation [110].

1.2.4.1 Solubility of Gas in Ionic Liquid Systems

As the vapor pressure of ionic liquids is very low, it is usually neglected, and the gaseous phase is assumed to completely consist of pure-gas component. Consequently, the VLE condition is only applied to that gas component. Its results can be correlated by the extended Henry's law:

$$k_{\mathrm{H,G}}(T,p)a_{\mathrm{G}}(T,m_{\mathrm{G}}) = f_{\mathrm{G}}(T,p) \tag{1.85}$$

where $k_{\mathrm{H,G}}(T, p)$is the Henry's constant of gas G in ionic liquid at temperature $T$and pressure p (based on the molality scale). $a_{\mathrm{G}}(T, m_{\mathrm{G}})$ is the activity of the gas in the ionic liquid, and the influence of pressure on that activity is neglected. $f_G(T, p)$ is the fugacity of the gas in the vapor phase.

The influence of pressure on Henry's law constant is expressed as:

$$k_{\mathrm{H,G}}(T,p) = k^{(0)}_{\mathrm{H,G}}(T)\exp\left(\frac{V^{(\infty)}_{m,G}p}{RT}\right) \tag{1.86}$$

where $k^{(0)}_{\mathrm{H,G}}(T)$ is the Henry's constant at zero pressure, $V^{(\infty)}_{m,G}$ is the partial molar volume of the gas at infinite dilution in the ionic liquid, and R is the universal gas constant.

The activity of the respective gas in the ionic liquid (on the molality scale) is

$$a_G = \frac{m_G}{m^o}\gamma_G \tag{1.87}$$

where m^o=1 mol · kg^{-1}. The activity coefficient a_G is calculated by employing the virial expansion for the excess Gibbs energy (also on the molality scale) according to Pitzer [111, 112]:

$$\ln\gamma_{\mathrm{G}} = 2\frac{m_G}{m^o}\beta^{(0)}_{\mathrm{G,G}} + 3\left(\frac{m_G}{m^o}\right)^2\mu_{\mathrm{G,G,G}} \tag{1.88}$$

Parameters $\beta^{(0)}_{\mathrm{G,G}}$ and $\mu_{\mathrm{G,G,G}}$ describe binary and ternary interactions, respectively, between gas molecules in the solvent.

The fugacity of the pure gas f_{G} at equilibrium temperature and pressure is the product of the total pressure p and the fugacity coefficient $\Phi_G(T, p)$

$$f_{\mathrm{G}}(T,p) = \mathrm{p}\Phi_{\mathrm{G}}(T,p) \tag{1.89}$$

The Henry's constant of the gas in ionic liquid at zero pressure $k^{(0)}_{\mathrm{H,G}}$(T) can be extrapolated from the experimental results.

$$k^{(0)}_{\mathrm{H,G}}(\mathrm{T}) = \lim_{p\to 0}\left[\frac{f_{\mathrm{G}}(T,p)}{m_{\mathrm{G}}/m^o}\right] \tag{1.90}$$