Physical properties of phosphonium ionic liquid and its mixtures with dodecane and water

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A B S T R A C T

Addition of molecular solvents, dodecane and water, to the hydrophobic phosphonium ionic liquid (IL) tetradecyltrihexylphosphonium bis-(2,4,4-trimethylpentyl)phosphinate decreases its density and viscosity significantly. These changes have been studied in the temperature interval between 15 and 60 °C and explained in terms of structural changes. Dependences of density and viscosity on the composition of binary and ternary systems are strongly nonlinear. Excess molar volumes and thermal expansion coefficients have been estimated for dry and water saturated solvents with IL. Strong H-bonding in water saturated solvents has been concluded from large negative excess molar volumes and strong temperature dependence of the density in water saturated solvents. VFT, Litovitz and Arrhenius models were tested for the correlation of temperature dependence of pure IL viscosity, showing that IL is a typical strong liquid. Deviations of the viscosity of the solvents to the ideal mixture viscosity based on the Eyring's theory of absolute rates were evaluated. In dynamic light scattering measurements, two different types of aggregates have been identified in the dry and water saturated solvents, with the mean size above 300 and 2 nm, respectively. High content of water of up to 8 molecules per ion pair of IL points to the existence of reverse micelles in the water containing solvents with hydrophobic IL.

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1. Introduction

Ionic liquids (ILs) are a new class of chemicals composed of ions, gaining attention of the research community as green replacements for traditional volatile organic solvents due to their unique physico-chemical properties, such as practically no vapor pressure. A disadvantage of pure ionic liquids is their rather high viscosity, posing a significant drawback in their possible application, *i.e.* in reactive extractions. Recently, hydrophobic ionic liquids (ILs) have appeared as promising new generation of reactive extractants for carboxylic acids. Especially phosphonium IL tetradecyltrihexylphosphonium bis-(2,4,4-trimethylpentyl)phosphinate, $[C_{14}C_6C_6C_6P][BTMPP]$, known as commercial product Cyphos IL-104 (Cytec, CA), exhibits excellent properties in LA and BA extraction as shown in papers [1–3]. Furthermore, this IL has practically no vapor pressure and high thermal stability, which allow its regeneration by short path vacuum distillation of acid at elevated temperatures [4]. Thermophysical properties of several phosphonium ILs with the $[C_{14}C_6C_6C_6P]$ cation were studied by Neves *et al.* in [5]. They observed a generally low impact of the water present on the density, while its significant impact on the viscosity of the ILs. Ferreira *et al.* [6] measured thermophysical properties of IL with a $[C_{14}C_6C_6C_6P]$

cation and a tris(pentafluoroethyl)trifluorophosphate anion. Experimental results with dicyanamide anion can be found in paper [7]. A prediction method of temperature dependence on the viscosity of ILs with a $[C_{14}C_6C_6C_6P]$ cation was proposed, knowing the viscosity of a specific IL at a given temperature. The effect of the alkyl substituent in ILs with phosphonium based cations on their viscosity was studied in papers [8–10]. Predictive methods for the estimation of thermophysical properties of ILs including viscosity are presented in paper [11]. Based on wide sets of experimental data, influence of the cation and anion structure on the IL viscosity was discussed in paper [12].

Formulation of the solvent for extraction processes combines tuning of its extractive and physical properties, especially viscosity, by diluent(s). Dodecane has been used to decrease the viscosity of $[C_{14}C_6C_6C_6P][BTMPP]$ in the extraction and pertraction of organic acids through supported liquid membranes containing IL in the membrane phase [1–3,13,14]. There are numerous studies on physical properties of the mixtures of ILs with various diluents, mostly with low molecular weight alcohols [15–21], polar organic solvents such as dimethylsulfoxide [22–25] or acetonitrile [21,23,26,27]. However, water immiscible diluents have to be applied for the application of IL containing solvents in L/L extraction from aqueous phase. Only scarce data on mixtures with water immiscible diluents are available. Furthermore, many ILs proven as good extractants of acids tend to contain a large amount of

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Nomenclature

A_A	parameter of Arhenius model, equation (3), Pa · s	$\Delta s^{\#}$	activation entropy, J · mol^{-1} · K^{-1}
A_{VFT}	parameter of VFT model, equation (4), Pa · s · K$^{-0.5}$	$\Delta s^{\#id}$	activation entropy for ideal mixture, J · mol^{-1} · K^{-1}
A_L	parameter of Litovitz model, equation (5), Pa · s	$\Delta s^{\#E}$	deviation of activation entropy, J · mol^{-1} · K^{-1}
B_{VFT}	parameter of VFT model, equation (4), K	T	temperature, K
B_L	parameter of Litovitz model, equation (5), kJ · mol · K^2	v	molar volume, m^3 · mol^{-1}
E_a	activation energy of Arrhenius equation, equation (3), J · mol^{-1}	v^E	excess molar volume, defined by equation (1)
G	interaction parameter of Grunberg and Nissan equation, equation (7), –	x	molar fraction, –
		X_{IL}	relative molar fraction of IL in dry portion of the solvent, defined by equation (18), –
$\Delta g^{\#}$	activation Gibbs energy, J · mol^{-1}	$\Delta z^{\#}$	parameter of the Eyring's model in general
$\Delta g^{\#id}$	activation Gibbs energy for ideal mixture, J · mol^{-1}	$\Delta z^{\#id}$	parameter of the Eyring's model in general for ideal mixture
$\Delta g^{\#E}$	deviation of activation Gibbs energy, J · mol^{-1}	$\Delta z^{\#E}$	deviation of parameter of the Eyring's model in general
h	Planck's constant, m^2 · kg · s^{-1}	α	thermal expansion coefficient, defined by equation (2), K^{-1}
$\Delta h^{\#}$	activation enthalpy, J · mol^{-1}		
$\Delta h^{\#id}$	activation enthalpy for ideal mixture, J · mol^{-1}	ρ	density, kg · m^{-3}
$\Delta h^{\#E}$	deviation of activation enthalpy, J · mol^{-1}	η	dynamic viscosity, Pa · s
M	molar mass, kg · mol^{-1}	η^E	excess dynamic viscosity, equation (6), Pa · s
N_A	Avogadro number, mol^{-1}	σ	standard deviation
R	universal gas constant, J · mol · K^{-1}		

water in the equilibrium, despite their strongly hydrophobic character [1–3,8,28]. It was observed earlier that the presence of water in ILs has significant impact on the viscosity of phosphonium ILs [2,3,5,29], as it is well known for many imidazolium ILs from the early study of Seddon [30].

Deeper understanding of the relation between physicochemical properties of systems containing phosphonium ILs and suitable diluents in the formulation of solvents and their composition is needed to optimize the ILs composition for the extraction process. The study of physicochemical properties can bring more insight in the structure and interactions in supermolecular structures of the aggregates present in ternary solvents containing water, IL and non-polar diluent, which can play a role in the chemistry of the extraction.

There are numerous studies on IL structures based either on theoretical quantum mechanics or on molecular dynamic (MD) simulation, as well as experimental studies using *e.g.* X-ray scattering [31–33]. Local structure heterogeneities in the range of several nm containing a continual polar phase network or isolated polar phases, depending on the side alkyl chains size [34], with charged heads of ions surrounded by non-polar domains containing aliphatic moieties were observed for ILs containing aliphatic chains in the cation and/or anion structure [35].

Depending on the polarity of the diluent used, it is incorporated preferentially in the polar or non-polar domains of the IL, as comes out also from the MD simulation in [34–36]. This has been confirmed also experimentally. Hexane and benzene occupy the non-polar domains of ILs, lower alcohols are partly present in both regions [37]. There are numerous theoretical and experimental studies on the interactions between ILs and water and on the structures formed by ILs, showing that the incorporation of the IL in polar domains is in agreement with the statements above [34,35,37]. In general, there is a strong ion–dipole interaction between ILs and water [28]. An atomistic study of the impact of water on the viscosity has shown initial hydration of the anion with water and the following formation of clusters of water. The IR and Raman spectroscopy experiments have confirmed such organization of water in micelle like formation in systems with [C$_4$C$_1$IM][BF$_4$-] [38]. Another theoretical simulation with [C$_2$C$_1$IM][ac] supported by experiments led to similar results considering the hydration of the anion by formation of strong H-bonds [39]. The effect of several diluents with different polarity on the viscosity of pyridinium and

phosphonium based ILs, showing largest effect of water, is presented in [29]. The authors explained this effect by the suppression of the ionic association by incorporation of water molecules between the polar heads, increase of their distance and weakening of the coulombic interactions by H-bonding. Effect of polarity of diluent on viscosity of mixtures with imidazolium based IL was studied in [21], generally confirming larger impact of more polar molecules on mixture viscosity.

Influence of dodecane diluents and water on the density and viscosity of phosphonium IL [C$_{14}$C$_6$C$_6$C$_6$P][BTMPP] in the temperature interval of 15 and 60 °C was studied in this work. These changes are related to the structures present in the solvents depending on their composition. Viscosity and density results were confronted with a dynamic light scattering study of the aggregates in the solvents. These data provide valuable information for the solvent composition optimization.

2. Models of data representation

2.1. Density

Based on the density measurements, several parameters are useful for the analysis of structural changes in the mixtures: excess molar volume, defined at certain composition, temperature and pressure;

$$v^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}), \tag{1}$$

where x_i is the molar fraction of individual components in the mixture, M_i is its molar mass, ρ is the density of the mixture and ρ_i is the density of individual components. The thermal expansion coefficient is defined as follows:

$$\alpha = \frac{1}{v} \left(\frac{dv}{dT} \right)_p, \tag{2}$$

where v is the molar volume and T is temperature.

2.2. Viscosity

Several models have been employed to correlate the temperature dependence of the viscosity of pure ionic liquids, most commonly: