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Thermodynamic modeling of hydrogen solubility in a series of ionic liquids

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ABSTRACT

In this study, the Perturbed Hard Sphere Chain Equation of State (PHSC EoS) has been employed to predict the hydrogen solubility in a series of ionic liquids. As ionic liquids have no vapor pressure and no critical parameters and as hydrogen is a light molecule which behaves like a perfect gas, simple cubic equations of state cannot be used for modeling of H_2 + ionic liquid mixture. Three main parameters of non-cubic PHSC EoS, i.e. (r) the number of segments per molecule, (σ) the distance between two molecules at zero potential and (ϵ) well-depth of potential between two non-bonded units have been calculated by regression of the experimental Pressure-Volume-Temperature (PVT) data points. The hydrogen solubility decreases with increasing temperature in [BMIM][BF₄], [BMIM][C₈SO₄], [EMIM][EtSO₄], [MDEA][Cl], and [N_{4,1,1,1}][Tf₂N], but inverse temperature effect is observed in [BMIM], [BMPY], [EMIM] and [HMIM][Tf₂N] as well as [BMIM][MeSO₄]. The binary interaction parameter which has been obtained from fitting of the equation of state with experimental hydrogen absorption data shows both the usual and the opposite trend of temperature effect as well.

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Introduction

Today, the excessive consumption of fossil materials has been led to entering of toxic gases such as CO₂ and CO to the environment. On the other hand, fossil fuels resources, i.e. gas, oil and their derivatives, have been declining over time. Hence, scientists and experts are looking for an alternative to these out of date fuels. Meanwhile, hydrogen as a future energy carrier has opened the door for CO₂-free mobility and power generation. The interest in hydrogen has been started by introduction of hydrogen powered fuel cells and by the demand of efficient energy storage for renewable electricity [1,2]. Hydrogen is an excellent candidate to supersede current fuels because of its high energy density and zero emission of

greenhouse gases. It shows the superiority that its combination with atmospheric oxygen produces energy and water as the only by-product. Despite this, there are still some disadvantages that prevent the proceeding of the so-called “hydrogen economy”. The first is the unavailability of this gas in pure form in the earth’s crust, then hydrogen must be produced in a usually unsustainable process. The second is the dangers related to its flammable nature and the requirements for its storage and transportation in a compressed way [3]. To meet the storage challenges, a host of associated performance and system necessities should be taken into account. Issues to be considered include operation pressure and temperature, the stability of the storage material, the degree of hydrogen purity imposed by the fuel cell, the reversibility of hydrogen uptake and so on [4]. Hydrogen can

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be stored as a compressed gas in high pressure tanks [5,6], as a liquid by absorbing physically and chemically within metal hydrides [7], carbon nanotubes [8] and metal organic frameworks [9] or by storing in an alternative chemical form. In fact the aforementioned requirements are in contradictory to each other and accordingly seems to be unattainable especially with compressed gas and liquid methods. Storing of hydrogen in chemical compounds offers a much wider range of possibilities to meet storage challenges. There is currently growing interest in gas storage by ionic liquids. Ionic liquids known as green solvent are a kind of salt that unlike high-temperature molten salts such as alkaline earth metal salts are liquid at room temperature. Their unique properties such as non-flammability, non-toxicity, high temperature stability and low vapor pressure makes them logical replacement for volatile organic solvents used in liquid membranes for separation processes [10]. Actually, as none of the present hydrogen purification technologies including pressure swing adsorption and cryogenic separation have reached level of industrial sophistication, an extensive amount of research have been carried out for development of supported liquid membranes whose pores are impregnated with ionic liquids (SILM). Then, reliable information on the solubility of hydrogen in ionic liquids is needed for the design and operation of separation processes [11]. The solubility of hydrogen has been investigated in a wide range of imidazolium-based ILs including 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] [12], 1-butyl-3-methylimidazolium octylsulphate [BMIM][C₈SO₄] and 1-ethyl-3-methylimidazolium methylsulfate [EMIM][EtSO₄] [13], 1-butyl-3-methylimidazolium hexafluoro-phosphate [BMIM][PF₆] [14–16], 1-butyl-3-methylimidazolium methyl sulfate [BMIM][MeSO₄] [17], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide [BMIM][Tf₂N] [18], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide [BMPY][Tf₂N] [19], 1-ethyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide [Emim][Tf₂N] [20], in 1-hexyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide [HMIM][Tf₂N] [21–23], 2-[2-hydroxyethyl(methyl)amino] ethanol chloride [MDEA][Cl] [24] and in butyltrimethylammoniumbis(trifluoromethylsulfonyl) imide [N_{4,1,1,1}][Tf₂N] [25].

The prediction of hydrogen solubility in ILs is a fundamental step toward the development of simulation tools to implement in the process calculation prior to industrial applications such as fuel cells and so on. Since the ionic liquids are complex macromolecules and they have no or small vapor pressure and consequently no critical parameters, simple cubic equations of state cannot be used for their modeling. On the other hand, hydrogen is a light gas with small intermolecular forces which cause hydrogen behaves like a perfect gas. Moreover, hydrogen solubility in ionic liquids, in contrast to conventional gases, does not always decreases with temperature. It shows a decreasing trend in a range of temperature and an increasing trend in another range of temperature. Thus, the purpose of this study is to correlate the unusual solubility behavior of hydrogen and to predict the amount of hydrogen sorption in ionic liquids. In this respect, hydrogen gas sorption in ILs has been modeled using Perturbed Hard Sphere Chain (PHSC) equation of state (EoS) in continuity of our previous research done for hydrogen storage in a series of Zn-

based Metal Organic Frameworks (MOFs) [26]. For this purpose, three main parameters of this equation including the number of segments per molecule (r), which is selected based on the size of each molecule relative to methane molecule, the distance between two molecules at zero potential (σ) and the well-depth of potential between two non-bonded units (ϵ) have been obtained from laboratory Pressure-Volume-Temperature (PVT) data points using the Differential Evolution (DE) optimization algorithm. One binary interaction parameter along with its corresponding mixing rule has been introduced in the equation of state for the mixture, to show the mutual influence of hydrogen and ionic liquid on each other.

Theory

The PHSC equation of state has been established based on the modified Chiew equation of state for hard-sphere chains as the reference term [27] which has been derived from Percus-Yevick integral-theory and modified by Carnahan-Starling radial distribution function. A van der Waals attractive term has been taken as perturbation part and the Song-Mason method [28] relates the parameters of the equation of state to the intermolecular potential.

The general form of PHSC EoS is written as below:

$$\left(\frac{P}{\rho k_B T}\right) = \left(\frac{P}{\rho k_B T}\right)_{ref} + \left(\frac{P}{\rho k_B T}\right)_{pert} \quad (1)$$

$$\left(\frac{P}{\rho k_B T}\right) = 1 + r^2 b g(d^+) - (r-1)[g(d^+) - 1] - \frac{r^2 a \rho}{k_B T} \quad (2)$$

where P is the pressure, T the absolute temperature, $\rho = N/V$ the number density and k_B the Boltzmann constant. d is the hard sphere diameter and $g(d^+)$ is pair radial distribution function of hard spheres which are at constant with each other. The three segment-based parameters, a , b and r which are interpreted physically, represent the strength of the attractive force between two non-bonded segments, the van der Waals segment co-volume and the number of single hard spheres per chain molecule, respectively. a and b are functions of temperature and can be correlated in terms of suitable reducing constants as follows [29]:

$$a = \left(\frac{2\pi}{3}\right) \sigma^3 \epsilon F_a \left(\frac{k_B T}{\epsilon}\right) \quad (3)$$

$$b = \left(\frac{2\pi}{3}\right) \sigma^3 F_b \left(\frac{k_B T}{\epsilon}\right) \quad (4)$$

$$F_a \left(\frac{k_B T}{\epsilon}\right) = 1.8681 \exp \left[-0.0619 \left(\frac{k_B T}{\epsilon}\right) \right] + 0.06715 \exp \left[-1.7317 \left(\frac{k_B T}{\epsilon}\right)^{\frac{3}{2}} \right] \quad (5)$$

$$F_b \left(\frac{k_B T}{\epsilon}\right) = 0.7303 \exp \left[-0.1649 \left(\frac{k_B T}{\epsilon}\right)^{\frac{1}{2}} \right] + 0.2697 \exp \left[-2.3973 \left(\frac{k_B T}{\epsilon}\right)^{\frac{3}{2}} \right] \quad (6)$$

F_a and F_b are the general functions of the reduced temperature as described for macromolecules [30]. The extended

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