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Effects of solubility properties of solvents and biomass on biomass pretreatment

Piyarat Weerachanchai [a], Sang Kyu Kwak [b], Jong-Min Lee [a,*]

[a] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore
[b] School of Nano-Bioscience and Chemical Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea

HIGHLIGHTS

- Hildebrand solubility parameter provides information to select a suitable solvent.
- The parameter of the mixture of EMIM-AC and organic solvent was investigated.
- The parameter of the mixture at different lignin contents was investigated.
- The parameter for biomasses is in the ranges of 25.14–26.11.

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ABSTRACT

Hildebrand solubility parameters of biomasses and pretreatment solvents were examined by a method of intrinsic viscosity. This is to be used as basic information in selecting a suitable solvent for biomass pretreatment processes. The effects of mixing1-ethyl-3-methylimidazolium acetate (EMIM-AC) and different solvents, lignin content in a pretreatment solvent, and biomass type on the Hildebrand solubility parameter and thermodynamic properties were carried out and calculated in this work. The Hildebrand solubility parameters of the mixtures are according to those of organic solvents: δ_H[EMIM-AC/DMA] = 25.07 < δ_H[EMIM-AC/DMF] = 25.48 < δ_H[EMIM-AC/DMSO] = 26.10 < δ_H[EMIM-AC/Ethanolamine] = 26.95. The Hildebrand solubility parameters of biomass compositions (microcrystalline cellulose, xylan and alkali lignin) and biomasses (cassava pulp residue and rice straw) vary in the ranges of 25.14–26.13. The increases of lignin content in the pretreatment solvents lead to the Hildebrand solubility parameter becoming closer to that of lignin.

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1. Introduction

Ionic liquids (ILs) have been attractive in a variety of industrial applications, including electrochemical applications, organic synthesis, catalysis and solvent extraction (Liu et al., 2005; Wei and Ivaska, 2008). They are addressed as environmentally friendly molten salts. They have a wide range of solubility in inorganic or organic compounds, low melting points, non-volatility, high thermal stability, recyclability and designability (Poole and Poole, 2010). These excellent properties are beneficial, especially the use of ionic liquids as a new class of solvents because they minimize solvent waste and reduce emission of hazardous vapors. Ionic liquids have gained overwhelming interest in improving a number of conventional processes, such as biomass pretreatment, drug delivery, liquid–liquid and gas–liquid partition system, gas storage, and handling applications (Feng and Chen, 2008; Martín-Calero et al., 2011; Poole and Poole, 2010). However, to investigate a suitable solvent for different applications, solvation characteristics and some fundamental properties such as density, viscosity, vapor pressure, conductivity, etc., should be considered. Several solvation properties, including empirical relationships of linear solvation energy (Abraham solvation model), Kamlet-Taft, Hildebrand and Hansen solubility parameters, have been used as important factors in predicting properties of materials or in selecting a favorable solvent (Mora-Pale et al., 2011; Poole and Poole, 2010). Nevertheless, Kamlet-Taft parameters and Hildebrand solubility parameters are the most wide spread and most commonly used to examine the solvent properties of ionic liquids (Mora-Pale et al., 2011; Poole and Poole, 2010).

The Hildebrand solubility parameter is a numeric value to indicate the strength of the molecular interaction between solvent molecules (Swiderski et al., 2004). It has been presented as an expedient parameter to determine a promising solvent for many

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* Corresponding author. Tel.: +65 65138129.
E-mail address: jmlee@ntu.edu.sg (J.-M. Lee).

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applications, such as film and tablet coating, wet granulation binders, drug permeation of skin, supported liquid membranes, and gas capture from mixture gases (Bustamante et al., 2005; Sistla et al., 2012). The Hildebrand solubility parameter (δ_H) is defined as the square root of the cohesive energy density (CED), the energy required to break the interactions between molecules (ΔU) per molar volume (V) which is equal to the square root of the difference of enthalpy of dissolution (ΔH) and ideal gas constant (R) timing with temperature (T) per molar volume (V) (Lee and Lee, 2005):

$$\delta_H = \mathrm{CED}^{\frac{1}{2}} = \left(\frac{\Delta U}{V}\right)^{\frac{1}{2}} = \left(\frac{\Delta H - RT}{V}\right)^{\frac{1}{2}} \qquad (1)$$

Various methods have been used to evaluate the Hildebrand solubility parameter (δ_H): heat vaporization (ΔH_V)–temperature data, group contribution, solubility measurement, osmotic pressure, swelling, intrinsic viscosity, etc. (Barton, 1975; Lee and Lee, 2005). Of these, the intrinsic viscosity has been widely applied as an effective approach for measuring the extremely low vapor pressure of non-volatile compounds, such as polymers and drugs (Bustamante et al., 1998; Lee and Lee, 2005). The Hildebrand solubility parameter of the solvent, which provides maximum value of the solute's intrinsic viscosity, is the Hildebrand solubility parameter of solute (Lee and Lee, 2005; Malpani et al., 2011). The maximum of intrinsic viscosity indicates a maximum mutual interaction between solvent and solute (Malpani et al., 2011).

The determination of the Hildebrand solubility parameter of an ionic liquid obtained from intrinsic viscosity has been successful in providing accurate values and good agreement with the values derived from several methods including the solvent dependence on bimolecular rate constant of Diels–Alder reactions, computationally-based technique and activation energy of viscosity (Lee and Lee, 2005; Marciniak, 2011). It was known that an ionic liquid structure is a critical factor in affecting the value of the Hildebrand solubility parameter. The ionic liquids, which possess different types of anion and cation, would contribute different polarities and have different molecular interaction forces (Lee and Lee, 2005; Marciniak, 2011). Generally, the solubility parameter decreases with increasing an alkyl chain length (Marciniak, 2011). The nature of anion also influences the Hildebrand solubility parameter: a high polarity of anion tends to give a high Hildebrand solubility (Swiderski et al., 2004).

In the application of using ionic liquid as a biomass pretreatment solvent, the type of ionic liquid, which affects directly its physicochemical properties, has shown to be the most important factor for the process (Zakrzewska et al., 2010). 1-Ethyl-3-methylimidazolium acetate (EMIM-AC) has been known as a promising ionic liquid for the biomass pretreatment process (Weerachanchai and Lee, 2013; Weerachanchai et al., 2012b). It shows better performance of lignin extraction among other ionic liquids and gives a higher sugar conversion at lower pretreatment temperatures. It was also found that, when EMIM-AC was mixed with some organic solvents (*N*,*N*-dimethyl acetamide (DMA), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO)), its properties still maintained and rendered a slightly higher sugar conversion and lignin extraction (Weerachanchai and Lee, 2013). Nevertheless, a much greater enhancement of biomass pretreatment among ionic liquids was obtained when a mixture of EMIM-AC/Ethanolamine (60/40 vol%) was used as a pretreatment solvent (Weerachanchai and Lee, 2013).

As mentioned above, it was observed that the types of solvent added to the ionic liquid presented a strong effect on the biomass pretreatment. Therefore, the understanding of the physicochemical properties of the mixtures (ionic liquid and organic solvent) would be useful to design or select a promising pretreatment solvent for the biomass pretreatment process. From our previous work (Weerachanchai et al., 2012a), it was found that the derived Hildebrand solubility parameters of different types of ionic liquid provided an informative result to realize their solubility potentials. However, there is scarce research on the studies of solubility parameters of ionic liquid-solvent mixtures. This has tempted us to investigate the Hildebrand solubility parameters of the mixtures to screen a favorable solvent for the biomass pretreatment. The Hildebrand solubility parameters of biomasses should also be examined to ascertain a proper solvent having close value with those of different biomasses because a similar solubility parameter of solvent and solute would provide a greater solubility (Malpani et al., 2011). Furthermore, the ionic liquid containing various lignin amounts, which was reported to show important effects on biomass pretreatment (Weerachanchai and Lee, 2014), should be measured for their Hildebrand solubility parameters to understand the effect of lignin content on the Hildebrand solubility parameters.

In this study, we focus on investigating the Hildebrand solubility parameters of mixtures of EMIM-AC and different solvents, pretreatment solvents which contain different amounts of lignin, and different biomasses, in order to use them as a key to select a suitable solvent for the biomass pretreatment process. The Hildebrand solubility parameters of all samples were determined by measuring the intrinsic viscosity at 25 °C. Moreover, their cohesive energy density, molar internal energy and enthalpy of dissolution (which were calculated from the Hildebrand solubility parameter), density, and molecular weight of interests were also investigated.

2. Methods

2.1. Chemicals

1-Ethyl-3-methylimidazolium acetate (EMIM-AC, $\geqslant$96.5%), and the analytical grade of used solvents possessing different Hildebrand solubility parameters including 2-butanol (22.2 $\mathrm{MPa}^{1/2}$), *N*,*N*-dimethyl acetamide (DMA, 22.7 $\mathrm{MPa}^{1/2}$), 1-butanol (23.1 $\mathrm{MPa}^{1/2}$), 2-propanol (23.5 $\mathrm{MPa}^{1/2}$), 1-propanol (24.5 $\mathrm{MPa}^{1/2}$), dimethyl formamide (DMF, 24.8 $\mathrm{MPa}^{1/2}$), nitromethane (25.1 $\mathrm{MPa}^{1/2}$), allyl alcohol (25.7 $\mathrm{MPa}^{1/2}$), ethanol (26.5 $\mathrm{MPa}^{1/2}$), dimethyl sulfoxide (DMSO, 26.7 $\mathrm{MPa}^{1/2}$), propylene carbonate (27.3 $\mathrm{MPa}^{1/2}$), 2-pyrrolidone (28.4 $\mathrm{MPa}^{1/2}$), methanol (29.6 $\mathrm{MPa}^{1/2}$), diethylene glycol (29.9 $\mathrm{MPa}^{1/2}$), ethanolamine (31.3 $\mathrm{MPa}^{1/2}$), and water (47.9 $\mathrm{MPa}^{1/2}$) were obtained from Sigma–Aldrich.

Biomass compositions consisting of microcrystalline cellulose, xylan from beech wood and alkali lignin (acquired from Sigma–Aldrich), and different biomasses of cassava pulp residue and rice straw, were prepared by milling and sieving to obtain particle sizes less than 38 μm. The fine particles of biomass compositions and different biomasses were dried at 120 °C for 24 h in an oven to speed up the removal of excess moisture prior to measuring their Hildebrand solubility parameters.

2.2. Determination of intrinsic viscosity

The intrinsic viscosities of ionic liquids, mixtures of the ionic liquid and an organic solvent, pretreatment solvent containing a different lignin amount and biomasses were measured by using Ubbelohde viscometers, in order to determine their Hildebrand solubility parameters (Lee and Lee, 2005; Weerachanchai et al., 2012a). The solutions of interest in different solvents were prepared for five concentrations varying 0.5–5% (v/v). The viscosities of solutions were examined by holding temperatures at 25 °C. The efflux times were measured at least 5 times (variation of efflux time being within 0.1 s). The intrinsic viscosity (g; dL/g) was determined from the common intercept of Huggins and Kraemer

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