Hildebrand solubility parameters of ionic liquids: Effects of ionic liquid type, temperature and DMA fraction in ionic liquid

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HIGHLIGHTS

- The type of ionic liquid presents the important effect on the solubility parameter.
- The influence of anion: \([\text{PF}_6]\) > \([\text{Tf}_2\text{N}]\) > \([\text{Cl}]\).
- The Hildebrand solubility parameters of the mixtures do not agree with the mixing rule.
- The increase of temperature from 25 to 60 °C results in the decreases of the parameters.

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ABSTRACT

The Hildebrand solubility parameters of 10 ionic liquids were investigated using the approach of intrinsic viscosity. Effects of dimethylacetamide (DMA) fraction in ionic liquids and dissolution temperature on the Hildebrand solubility parameter were also studied. Moreover, cohesive energy density, molar internal energy and enthalpy of dissolution were calculated. Cation and anion of an ionic liquid shows a significant influence on the solubility parameter. The values of ionic liquids containing BMIM cations are in the following order: \([\text{PF}_6]\) > \([\text{Tf}_2\text{N}]\) > \([\text{Cl}]\), while those of ionic liquids containing EMIM cations are in the order: \([\text{BF}_4]\) > \([\text{DEPO}_4]\) > \([\text{AC}]\). Ionic liquid containing HOEMIM exerts the highest solubility parameter than that containing MBPYRRO or BMIM. Considering effect of varying DMA fraction, the Hildebrand solubility parameters of the mixtures do not correspond to the mixing rule. Their values tend to be closer to those of the ionic liquids than that of DMA for 40–90 vol% DMA added in the ionic liquids (1-Butyl-3-methylimidazolium chloride (BMIM-Cl)). With increasing temperature from 25 to 60 °C, decreases of Hildebrand solubility parameters from 25.2 to 24.7 for EMIM-AC and the mixture of EMIM-AC/DMA (60–40 v/v) were obtained. The cohesive energy densities of ionic liquids at the different conditions are proportional directly with the Hildebrand solubility parameter. The molar internal energy and the enthalpy of dissolution decrease with increasing DMA fraction in ionic liquids, while they are almost constant or show slight decreases with the increase of dissolution temperature for EMIM-AC and the mixture of EMIM-AC/DMA (60–40 v/v), respectively.

1. Introduction

Solubility parameter is a numeric value to indicate the strength of molecular interaction between solvent molecules [1]. It has been shown as a useful factor in determining and predicting the fundamental properties of material such as solubility and swelling of polymers by solvents, and/or being an effective screening tool for selecting a favorable solvent for many applications, such as film coating, tablet coating and wet granulation binders, drug permeation to skin, supported liquid membranes, and gas capture from mixture gases [2–8]. A solute is soluble in solvents which have a similar solubility parameter [2]. The concept of the solubility parameter which is related to the internal energy of a solvent and a solute was first proposed by Hildebrand. The Hildebrand solubility parameter \((\delta_H)\) is defined as the square root of the cohesive energy density \((\text{CED})\), the energy required to break the interactions between molecules \((\Delta U)\) per molar volume \((V)\) which is equal to the square root of the difference of enthalpy of dissolution \((\Delta H)\) and ideal gas constant \((R)\) timing with temperature \((T)\) per molar volume \((V)\) [2,9,10]:

\[
\delta_H = \text{CED}^{\frac{1}{2}} = \left(\frac{\Delta U}{V}\right)^{\frac{1}{2}} = \left(\frac{\Delta H - RT}{V}\right)^{\frac{1}{2}}
\]