흡수식 냉동기에 사용되는 이온성 액체의 작동유체로서의 응용

김기섭, 이흔
한국과학기술원 생명화학공학과

Ionic Liquids as Working Fluids for Absorbtion Chiller

Ki-sub Kim and Huen Le
Dept. of Chemical and Biomolecular Eng. KAIST

Introduction

The absorption heat pump has received growing attention in the past years from the areas of air-conditioning and refrigeration, especially in the aspect of energy saving and the protection of environment. At the present time, ozone depletion and the concomitant regulation of CFC refrigerants has created an interest in non-ozone-depleting refrigerants for use in commercial sized chillers. Present CFC refrigerants need to be replaced by environmentally benign refrigerants based on fluoroalcohols. Also, a heat-driven cooling technology has been developed to reduce the demand of electric power.

Absorption heat pump transfer the heat from a low temperature to a high temperature with the help of thermodynamic input in the form of heat. It is the technology related to heating or cooling cycle which uses an absorbent-refrigerant pair as a working fluid and the heat as energy source.

The performance of an absorption heat pump are determined to a large degree by the properties of the working fluids. Until now, H_2O + LiBr and NH_3 + H_2O have been the most widely used working pairs for absorption heat pump systems. However, they still have critical disadvantages, which are corrosion and solubility problems for H_2O + LiBr and high working pressure and toxicity for NH_3 + H_2O. Though various organic working fluids have been suggested to improve the defects of conventional working fluids, their volatility and low coefficient of performance (COP) have become new problems.[1]

Ionic liquids have been extensively studied as battery electrolytes and solvent alternatives owing to their unique chemical and physical properties. Recently, we have investigated that ionic liquids could be environmentally friendly absorbents with fluoroalcohol to overcome all disadvantages of classical working fluids, which includes LiBr + H_2O, NH_3 + H_2O and organic absorbents + fluoroalcohols mixtures.

Room temperature ionic liquids are liquids that are composed entirely of ions, and in this sense alone resemble the ionic melts which may be produced by heating normal metallic salts such as sodium chloride to high temperature (e.g. NaCl to over 800℃). In fact, ionic liquids can now be produced which remain liquid at room temperature and below (even as low as -96℃) and appear to be undemanding and inexpensive to manufacture. Ionic liquids based on methylimidaxolium are favorable species for investigation because of their air and water stability, their wide liquids range, the fact that they remain liquid at room temperature, and their relatively favorable viscosity and density characteristics. In addition, the length of side chain of the cation is variable and may be used to fine tune the properties of the ionic liquid.[2]

In this study, we first report application of ionic liquids to working fluids used in an absorption chiller. 1-Butyl- 3-methyl imidazolium tetrafluoroborate ([bmim][BF_4]) + 2,2,2 -trifluoroethanol (TFE) and 1-butyl-3-methyl imidazolium bromide ([bmim][br]) +TFE mixtures were chosen as a potential working fluids. Ionic liquids act as absorbents and TFE acts as a refrigerant. TFE has good solubility in the suggested ionic liquids because of their permanent ion-dipole interaction. It is also worthwhile to note that these two organic chemicals can be easily separated by a heat source because ionic liquids have not detectable vapor pressure and TFE is volatile.

To optimally design an absorption heat pump and decide whether each of the ionic liquid + TFE system is suitable as a new working pair for absorption heat transformers or not, vapor pressures and heat capacities of the working fluids were measured. The thermodynamic properties treated in this study can be a useful information for the design of the absorption heat pump.

Experimental

Vapor pressure : The boiling point method was used to measure the vapor pressures. The vapor pressure measuring apparatus primarily consists of an equilibrium vessel (100 cm3), a constant temperature bath, a condenser, a U-tube mercury manometer capable of being read to 0.05 mm, a K-type thermocouple, and two stirrers. A sample solution of a desired absorbent concentration was first placed in the vessel, and the system was evacuated to a slightly higher pressure than the expected vapor pressure of the sample solution at the initial temperature. Then the sample solution was heated and stirred well with a magnetic stirrer to prevent superheating. After thermal equilibriumwas reached, the temperature of the sample solution and the pressure were measured.

Heat capacity : A differential scanning calorimeter was used for the measurements. The calorimeter was calibrated by measuring the heat capacities of a standard sample synthetic sapphire at different temperatures; the maximum deviation from the standard data was within 1.5%. A smple of 5mg was placed in a stainless steel sample container, which was then placed in the calorimeter. Meanwhile another empty container ofthe same size was put in the calorimeter as a reference.

Result and Discussion

The vapor pressure data were in general needed to analyze an absorption heat pump cycle along with the heat capacity data. The vapor pressures of the ionic liquid + TFE system were measured by using a boiling point method in the concentration range from 40 to 90 mass percent of ionic liquid. The experimental results are listed in Figures 1, 2, and 3 and these values were correlated with an Antoine-type equation which expresses vapor pressure as a function of temperature and concentration:

$$\log P = \sum_{i=0}^{3} [A_i + 1000 B_i / (T - 43.15)] X^i \quad (1)$$

where P is the vapor pressure in kPa, Ai and Bi the regression parameters, T the absolute temperature in K, and X the concentration of refrigerant (TFE). The parameters Ai and Bi were determined by a least-square method. These figures show that the log P vs. 1000/(T-43.15) relation at a given concentration appeared to be linear over the pressure and temperature ranges considered.

Heat capacities of each of the pure ionic liquid were measured over the range of 298.15K to 323.15K. The experimental results are plotted in Figure 4. The heat capacities of the pure ionic liquids increased with increasing temperature.

Conclusion

[Bmim][BF_4] + TFE and [bmim][Br] +TFE systems were selected as a new working fluids for use in absorption heat pump in this study. For the proper cycle analysis both vapor pressures and heat capacities were accurately measured over wide concentration and temperature ranges. The data set for vapor pressure was fitted with an Antoine-type equation. Both systems were found to be possibly used as new working fluids for an air-cooled absorption chiller. For the practical application of the selected solutions to real working fluids, additional studies on the corrosion problem, heat and mass transfer characteristics, cost evaluation, and son on should be further carried out.

Reference

1. Kim, K.S., Lee, H. J. Chem.Eng.Data, 47,216-218, 2002
2. Jonathan G. Huddleston, Heather D. Wilauer, Richard P. Swatloski, Ann E. Visser and Robin D. Rogers . Chem.Comm 1765-1766, 1998

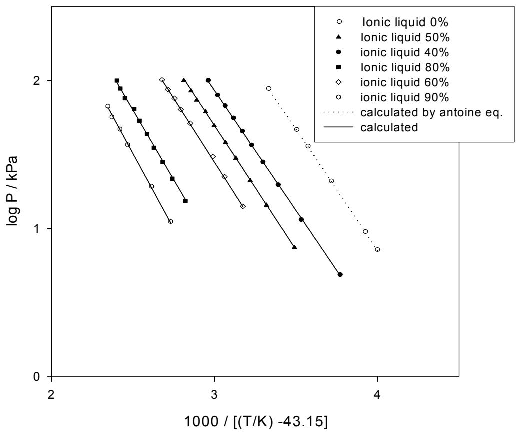

Fig 1. Vapor pressures of [bmim][BF4] + TFE

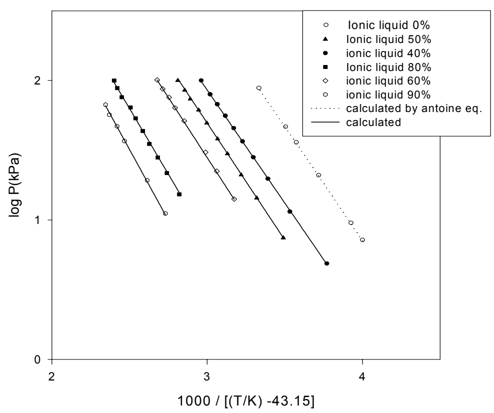

Fig 2. Vapor pressures of [bmim][Br] + TFE

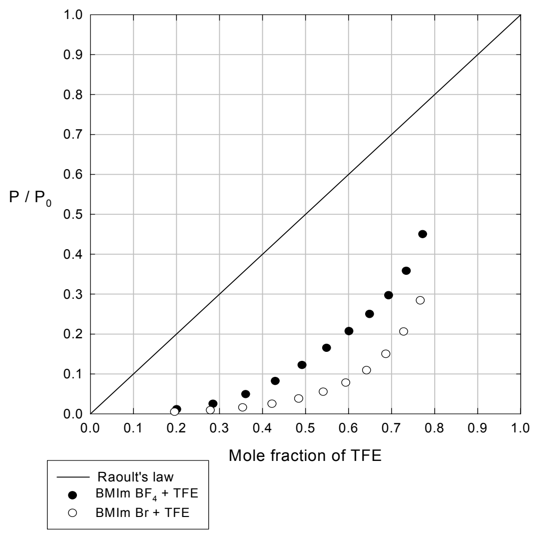

Fig 3. The comparison vapor pressures between [bmim][BF4] + TFE and [bmim][Br] + TFE

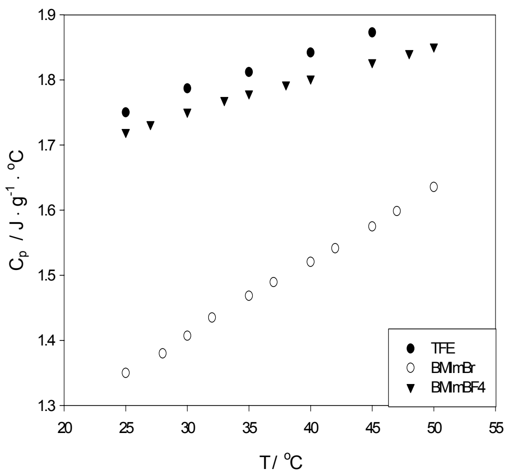

Fig 4. Heat capacities of TFE, [bMIm][BF4], and [bmim][Br]