MEASUREMENT AND PREDICTION OF FUEL OXYGENATES MIXTURES EXCESS THERMOPHYSICAL PROPERTIES - A REVIEW

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ABSTRACT
Excess thermophysical properties are important in understanding the molecular interaction between unlike molecules. The excess properties data are very important for process design and separation, especially in chemical industry. The excess thermophysical properties reviewed are excess molar volume, excess molar enthalpy and viscosity. In this review, particular interest is taken on binary mixtures of fuel oxygenates which are methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) with lower alcohols. This review will enable researchers to know what are the mixtures studied and where future work is required.

Keywords: Excess properties • Fuel oxygenates • Ether • Binary mixture •

INTRODUCTION

The excess thermophysical properties of binary oxygenate mixtures are of much importance in the petrochemical industry. Oxygenated compounds like ethers and alcohols have become a very important gasoline additive in substituting tetraethyl-lead. This is due to their good anti-knocking properties. Various tertiary-alkyl ethers have been suggested as fuel additives that both alone or with other ethers or alcohols can enhance the octane rating and reduce pollution effects arising out of the combustion process. The function of oxygenates is to enhance the octane rating of internal combustion engines and to reduce air pollution by ensuring a more complete fuel combustion in the engines. Arteconi *et al.* (2011) stated the addition of oxygenates improves the fuel's chemical composition and physical properties without modifying engine's characteristic. In United States, the reduction of lead in gasoline came in response due to two important factors which are the mandatory use of unleaded gasoline to protect catalytic converters in all cars starting with the 1975 model year and increased awareness of the negative human health effects of lead, leading to the phasedown of lead in leaded gasoline in the 1980s (Newell and Rogers, 2003). This has led to numerous research to investigate the thermophysical properties of oxygenates.

Marsh *et al*. (1999) have done the detailed review on thermophysical properties of ether and hydrocarbon mixtures (Marsh *et al*., 1999). However, there is no review done yet on the ether and alcohol mixture. In this review, the excess molar volume, excess molar enthalpy and viscosity properties will be discussed for MTBE, ETBE, and TAME binary mixtures.

Fuel Oxygenate Additives

The two main classes of oxygenated additives are tertiary alkyl ethers and alcohol. Tertiary alkyl ethers are environment friendly oxygenates and are widely being used as octane enhancer for gasoline. According to Paroma *et al.* (2004), the high octane level of tertiary alky ethers enables them to replace aromatics in the fuel which are responsible for high emissions of carbon monoxide and hydrocarbons. Gasoline burns more completely in the presence of oxygen, in return reducing motor vehicles exhaust emissions. Some of the common tertiary alkyl ethers that can be used as gasoline additive are methyl-tert-butyl ether, ethyl-tert-butyl ether, and tert-amyl methyl ether. Methyl-tert-butyl ether is widely used as gasoline additive since 1975 replacing tetraethyl lead to increase octane rating and reduce engine knocking. This is due to its high octane level, low cost feedstock, ease of blending with gasoline, and ease of transfer and distribution (Deeb *et al*., 2003). Some of the alcohols used as gasoline additive are methanol, ethanol, isopropyl alcohol and n-butanol. They are not favoured because of several drawbacks of alcohols such as their high Reid vapour pressure (RVP). Due to increased vapour pressure, they cause clogging of the fuel flow. Alcohols are also highly soluble in water causing problems in phase separations. (Arteconi *et al.*, 2011).

Nevertheless, the study of alcohol and ether mixtures are emerging as it is believed that binary mixtures of ether and alcohol can give better performance in gasoline compared to just using ether alone or alcohol alone (Blanco *et al*., 1996). In a number of papers, it have been discussed that it is due to their complex structure formed by alcohol and ether„ a consequence of the self-association of the alcohols, which is particularly destroyed by the active ether molecules, and on the new intermolecular OH-O bonds created (Hoga and Tôrres, 2011; Mato *et al*., 2008).

Excess Thermophysical Properties

Physiochemical properties measurement are very important in the fundamental understanding of the nature of interactions between unlike molecules. Excess properties have been a qualitative and quantitative way to predict the deviation from ideal behaviour of liquid binary mixtures compared to experimental data. From a more