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 tetaethyl-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 alkyl 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 either 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 Törres, 2011; Mato et al., 2008).

Excess Thermophysical Properties

Physicochemical 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 fundamental point of view, thermodynamics are necessary for the understanding of the complex molecular interactions and mechanisms of solution. (Hoga and
The data of these thermophysical properties are very important in many chemical engineering calculations involving fluid flow, heat and mass transfer. The knowledge of dependency of volumetric and viscometric properties at different temperatures is required for process design and operation. Gonzalez-Olmos and Iglesias (2008), stated that testing of existing models and the development of new methods for prediction of these thermodynamic functions have a particular importance since they are the only way to ensure accurate results. Thus, the experimental and theoretical investigations of the excess thermodynamic properties of binary mixtures are of considerable interest.

From a thermodynamic point of view, under various temperature and pressure conditions, experimental property studies of binary mixtures can provide valuable information about the fluid behaviour. For proper design of synthesis and separation processes, the phase behaviour and thermodynamic properties of the fluid mixtures involved need to be known (Rezanova et al., 1999). There is always an existing need to have accurate density and viscosity data of liquids to develop new theories that probe the interactions between molecules of dissimilar size and polarity.

**Excess Molar Volume Methyl tert-butyl ether, MTBE**

Blanco et al. (1994) studied on branched ethers and lower alcohols which can be used for the improvement of gasoline performance. They were the first to produce a systematic thermodynamics properties study for the mixtures of ether and alcohol to improve gasoline performance. They have reported on excess volumes of binary mixtures formed by methanol, ethanol, propan-2-ol, diisopropyl ether (DIPE), methyl tert-butyl ether (MTBE) and 2, 2, 4-trimethylpentane at 298.15K. The excess molar volume data were fitted with ordinary least square method. They have found that the mixture of alcohol and ether shows negative value. They have concluded that 1-alcohol with branched alkane shows lower excess volume than alkane mixtures whereas branched alkane with branched alcohol and branched ether shows higher excess volume than that of linear ether and n-alcohol mixtures.

Excess molar volume of alkanol and branched chain ether were investigated by Letcher and Govender (1997) at temperature of 298.15K using MTBE, TAME, and IPE with methanol, ethanol, 1-propanol and 2-propanol. The excess molar volume curves were found to be negative and increases in the order of DIPE<MTBE<TAME which is due to the structure of the three ethers. MTBE and TAME have three methyl group packed around one carbon group resulting them to have stronger intermolecular congestion compared to that of DIPE which leads to lower availability of O in ether to interact with OH in alcohol. This effect increases with higher branching of ethers.

Excess properties of MTBE binary mixtures were studied with methanol, ethanol, 1-propanol and 1-butanol at temperatures 298.15K and 313.15K (Park et al., 2002). They have used correlated Redlich-Kister equation to calculate the partial excess molar properties at infinite dilution. Park et al., (2002) reported negative values for excess molar volume of MTBE and alcohol binary mixtures. Their findings support the results that were found by the previous researchers.

A study on volumetric and viscometric properties of binary mixtures of MTBE with alcohols which are methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, or 1-hexanol at temperatures of 293.15K, 298.15K, 303.15K and 308.15K were done by Hoga and Torres (2011). Redlich-Kister polynomial equation was used to correlate the data of excess molar volume and viscosity deviation. The findings of Hoga and Torres is also similar to that of the previous studies with negative values of excess molar volume over entire range of composition.

**Ethyl tert-butyl ether, ETBE**

Oh and Park (1998) have examined the excess molar volume of ethyl tert butyl ether (ETBE) and alcohol mixtures of methanol, ethanol, and propanol at room temperature. Redlich-Kister model was used for correlation of the excess molar volume data. The value of excess molar volume is negative for all mixtures of ETBE and alcohol (Oh and Park, 1998).

Another study was done by Gonzalez-Olmos and Iglesias (2007) on ETBE and hydrocarbon mixtures which include alcohol, alkane and organic hydrocarbons at temperature range of 288.15K to 323.15K and pressure of 0.1 MPa. ETBE binary mixtures was explored with ethanol, tert butyl alcohol, isooctane, benzene, toluene, and ethylbenzene. They have analysed the excess volumes and deviation of isentropic compressibilities data in terms of different theoretical models. Redlich-Kister equation was used for correlation of the the derived properties.

**Tert-amyl methyl ether, TAME**

Pal and Dass (1999) have predicted excess molar volume of MTBE and TAME with alcohol system. Their findings are similar with other researchers whereby they get a negative value for excess molar volume for all the ether and alcohol mixtures but the alcohol and TAME mixture shows less negative value compared to that of MTBE and alcohol mixture. The reason for this behaviour was because of the placement of CH₂ molecule in middle of MTBE causes less volume contraction resulting a more excess molar volume of MTBE binary mixture than that of TAME mixture. Their findings supports the earlier findings of Letcher and Govender that molecular structure of a component affects the bond formation of ether and alcohol.

Excess molar volumes of binary mixtures of tert-amyl methyl ether (TAME) with methanol was studied at room temperature and pressure. The values of excess molar volume were found to be negative. (Kammerer et al., 2000). Their results also support previous findings of Pal and Dass.
Rezanova et al. (2000) have conducted an investigation on excess molar volume of TAME with ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, or 1-octanol. The correlation of data was done using Redlich-Kister equation. For the entire range of composition, the excess molar volume was found to be negative for all TAME and alcohol mixtures. From the findings of Rezanova et al. (2000), it was concluded that the molecular structure of the components affects the formation of the ether and alcohol bond. Linear alcohols have more pronounced formation of cross associates compared to that in branched alcohols. These findings by Rezanova et al. (2000) supports the previous findings of Letcher and Govender (1997).

The excess molar volume for all ether and alcohol mixture shows negative value. This is due to the hydrogen bond formation between the ether and alcohol molecules. The excess volume is higher for mixtures that have branched carbon compared to the linear mixtures. This is proven by the theory of Letcher and Govender (1997) that the more packing of methyl group around a carbon, the stronger the intermolecular congestion where there is lower availability of O to bond with OH in alcohol.

The effect on excess molar volume is caused by three type of interaction between the molecules in the mixture. The three type of interactions are physical interaction, chemical interaction and structural contribution. A positive contribution is caused by physical interaction between the molecules mainly due to the forces of dispersion between the mixture molecules, whereas a negative contribution results from chemical interaction whereby there is transfer in charge when H bonds are formed or when there is complex forming interactions. A negative contribution is also due to the structural contribution which is due to the difference is the shape and size of the mixture components. When the components are fitted into the structure of each other, the components volume and compressibility is reduced. This is the cause for the negative contribution. (Mahajan and Mirkane, 2013)

Excess Molar Enthalpy Methyl tert-butyl ether, MTBE

Tusel-Langer et al. (1991) have researched on excess molar enthalpy of MTBE with methanol. They have found S-shaped dependence on the composition at low compositions of MTBE with methanol binary mixture. They could not describe the reason for this behaviour.

Positive excess molar enthalpy values for MTBE and alcohol binary mixtures were reported from the findings of Tamura et al. (2001). They have discussed positive and negative factors affecting the excess molar enthalpy values. The positive factors were the hydrogen bonds disruption in the alcohol and steric effect of the mixture components. The OH group in the alcohol causes the stretching of hydrogen bonds in the alcohol. The molecules of the component was hindered by steric effect from coming close to each other due to geometrical factor. The negative factors discussed by them were that formation of complex between MTBE-alcohol molecules and free volume changes in mixture. Their experimental results show the positive factors outweigh the negative ones which mainly is due to restriction on extent of interaction between the mixture which is because of the sterically hindered molecules of MTBE. The results of the excess molar enthalpy supports that of Tusel-Langer in 1991 but Tamura et al. have come with the reasons that contribute to this behaviour in excess molar enthalpy.

The findings of Cebreiro et al. (2002) reported positive excess molar enthalpy values for all MTBE with alcohol mixtures except at low concentrations of MTBE in methanol which showed negative excess molar enthalpy values. The alcohols examined was methanol, ethanol ,1-propanol and 1-pentanol at temperature of 298.15 K. Cebreiro et al. suggests this phenomena is caused due to breaking of hydrogen bond in the alcohol is more dominant instead formation of new bonds during the mixing process. This happens only when the MTBE is weaker than the alcohol, which in this case is at low composition of MTBE in the mixture.

Morris et al. (1975) have derived an expression for excess molar enthalpy of acetone-chloroform-methanol binary and ternary mixtures. This expression was used by Mato et al. (2008; 2010) to predict the excess molar enthalpy of MTBE and alcohol binary mixtures system in their study. The effect of increasing chain length of alkanol on the excess molar enthalpy of MTBE and 1-alkanol mixture were analysed using C1 to C5 alcohol. Excess molar enthalpy values increases from methanol, ethanol and 1-propanol but remain constant for butanol and pentanol. The findings of Mato et al., (2010) suggested the reason for this is because of weaker interaction between OH and O group balanced the decrease in the alcohol.

Ethyl tert-butyl ether, ETBE

To the best of our knowledge, there were no literature found on excess molar enthalpy of ETBE and alcohol binary mixtures.

Tert-amyl methyl ether, TAME

Investigation on excess molar enthalpy of TAME binary mixtures with ethanol was conducted by Tong et al. (1996). Positive excess molar enthalpy values were reported for the ether alcohol mixtures, but no further discussion was made on the reasons for this behaviour.

From the findings of Rezanova et al. (2000), excess molar enthalpy values were found to be positive for TAME binary mixtures of ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-octanol. They have discussed the reason for this is breaking of the hydrogen bonds in the alcohol.

For all binary mixtures of ether and alcohol molecules, the excess molar enthalpy values was found to be positive. The reason for this is mainly due to the
destruction of hydrogen bonds in alcohol molecule when mixed with ether molecules.

**Viscosity Methyl tert-butyl ether, MTBE**

Viscosity results of MTBE and TAME with methanol, 1-propanol and 1-pentanol were analysed by Pal and Dass (1999). Viscosity deviation was found to be negative for all the systems except for methanol mixture with MTBE or TAME which shows positive sign. They have found the increase in value of viscosity deviations with increasing chain length of alcohols. The interaction strength is not the only factor affecting values of viscosity deviation. The molecular structure of the components is also another factor that affects viscosity deviation.

Another research on viscosity study of MTBE with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol or 1-hexanol was conducted by Hoga and Torres (2011). Negative viscosity deviation values were reported from their findings. 1-hexanol has larger negative value and reducing in the order 1-pentanol, 1-butanol, 2-propanol, 1-propanol and ethanol. They have said that the reason for the negative viscosity is when MTBE is mixed with the alcohol, the cohesive forces of the alcohol is reduced causing the alcohols to dissociate especially in large alcohols, the destruction happens in random resulting large negative value of viscosity deviation. Hoga and Torres have also found at increasing temperature, negative values of viscosity deviation decreases. This phenomenon is because of the increase of thermal energy at increasing temperature resulting in decrease in the association of the alcohol molecules.

Viscosity of MTBE and ethanol mixtures have been analysed Budeanu et al. (2014). Their findings support the findings of Hoga and Torres (2011).

**Ethyl tert-butyl ether, ETBE**

Viscosity of ethyl tert-butyl ether with n-ethoxyethanol mixtures were explored by Cwiklińska et al. (2007). They have used 2-ethoxyethanol (EE), 2-(2-ethoxyethoxy) ethanol (DEE) and 2-[2-(2-ethoxyethoxy) ethoxy] ethanol (TEE). Negative viscosity deviation values were reported for all the systems and the value becomes more negative at increasing of –O-CH$_2$-CH$_2$- group in the alkoxyethanol. They have discussed the negative viscosity deviation is due to the association between the ether and alcohol molecules. This findings supports to that of previous findings for MTBE and alcohol mixture by Hoga and Torres.

To the best of our knowledge, there was only one findings found on the viscosity study of ETBE with alcohol binary mixtures.

**Tert-amyl methyl ether, TAME**

There is no viscosity results found for TAME and alcohol binary mixtures except for the findings by Pal and Dass (1999) which have been discussed earlier.

Viscosity deviation for all the ether and alcohol binary mixtures shows negative deviation which is mainly due to the intermolecular forces of attraction between the ether-alcohol complexes.

**Nonlinear models used for Excess Thermophysical Properties in Fuel Oxygenate Binary Mixtures**

**Excess Molar Volume**

Excess volume for binary mixtures of MTBE and TAME with alcohol was fitted by Pal and Dass (1999) using Redlich Kister equation. Redlich Kister nonlinear model is the most commonly used model for correlating excess volume ($V^\text{e}$), excess enthalpy ($H^\text{e}$) and viscosity deviation ($\Delta \eta$) data of binary liquid mixtures (Redlich-Kister, 1948). The Redlich Kister equation is shown in equation 1 below.

$$Y = \sum_{i=1}^{k} A_i(x_1 - x_2)^{i-1}$$

where

- $x_1$ = mole fraction of mixture 1,
- $x_2$ = mole fraction of mixture 2,
- $A_i$ = polynomial coefficients, obtained by fitting experimental results with least square regression,
- $Y$ = refers to excess volume, excess enthalpy or viscosity deviation
- $k$ = number of the estimated parameters

Pal and Dass have obtained a standard deviation in the range of 0.002, 0.003 and 0.003 for excess volume for mixtures of MTBE with methanol, 1-propanol and 1-pentanol, respectively. For mixtures of TAME with methanol, 1-propanol and 1-pentanol, they have obtained standard deviation of 0.002, 0.002 and 0.003 respectively.

Standard deviations of 0.0068, 0.0048, 0.0097 and 0.0054 was obtained for MTBE mixtures with 1-propanol, 2-propanol, 1-butanol and 2-butanol. (Park et al., 2002). Both of this studies were carried out at room temperature of 298.15K. Standard deviation obtained for MTBE mixtures with 1-propanol is slightly higher than that obtained in Pal and Dass.

Hoga and Torres have predicted the excess molar volume of MTBE mixtures with alcohol using Redlich Kister model. They have obtained standard deviation of 0.0043 for MTBE and methanol mixture at 298.15K. For MTBE with 1-propanol mixtures at same temperature, they obtained standard deviation of 0.0062. In comparison with the standard deviation values obtained by Pal and Dass for mixtures of MTBE with methanol and 1-propanol, the values obtained by Hoga and Torres is slightly higher. The values of standard deviation obtained by Park et al. for MTBE with 1-propanol mixture is 0.0068, which is slightly similar with the value obtained by Hoga and Torres. Nevertheless, the standard deviation of the earlier prediction of Pal and Dass is lower than both of this recent studies.

Excess molar volume of TAME mixture with alkanols was fitted using Redlich Kister equation by
Rezanova et al. (2000). For the mixtures of TAME with ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-octanol, standard deviations of 0.0014, 0.0016, 0.0011, 0.0015, 0.0012 and 0.0017, respectively. By comparison of standard deviation values with those obtained from Pal and Dass for TAME mixtures with 1-propanol, it can be observed the standard deviations in Rezanova et al. is slightly smaller with only a difference of 0.0004. Both the correlations of Rezanova et al. and Pal and Dass is almost similar.

A standard deviation of 0.0161, 0.0083, 0.0160 and 0.0130 was obtained for excess molar volume fitted using Redlich Kister for ETBE binary mixtures with methanol, ethanol, 1-propanol and 1-butanol, respectively (Oh and Park, 1998). In a study by Gonzalez Olmos (2007) for ETBE and alcohol binary mixtures, standard deviation of 0.014 was observed when excess volume was correlated using Redlich Kister equation. This value is slightly higher when compare with the standard deviation obtained by Oh and Park.

For correlation excess molar volume data, it was found that only Redlich Kister nonlinear model was used for the binary fuel oxygenates mixture.

Excess Molar Enthalpy

Tusel-Langer et al. (1991) used Redlich-Kister equation (1) to fit $H^\theta$ data for MTBE-methanol binary mixtures. They have obtained standard deviation of 1.8, 3.2 and 2.7 for temperatures 298.15, 313.15 and 323.15 K, respectively. A standard deviation of 3 was obtained for the same mixtures at 298.15 K by Cebreiro et al. (2002). They have used 6 coefficients of $A_i$ whereas Langer et al. have stated that only 5 coefficients was necessary for a good fit of the excess enthalpy data. Standard deviations obtained by Langer et al. is smaller than that of Cebreiro et al., which indicates that using 5 coefficients for $A_i$ gives high precision compared to using 6 coefficients.

Rezanova et al. (2000) has also fitted viscosity deviation of TAME mixtures with Redlich Kister equation. They have obtained standard deviations of 1.2, 1.4, 1.3, 1.7, 1.5 and 1.6 for TAME mixtures with methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-octanol, respectively.

Viscosity Deviation

Redlich Kister equation is also widely used to correlate viscosity deviation data. Aside from Redlich Kister model, Hind, Grunberg-Nissan, Auslander and McAllister nonlinear models are also used for correlation of viscosity deviation.

Pal and Dass (1999) have used Redlich Kister equation to correlate the viscosity deviation for MTBE and TAME mixtures with alcohols. Standard deviations of 0.002, 0.003, and 0.003 was obtained for MTBE mixture with methanol, 1-propanol and 1-pentanol, respectively. Values of 0.002, 0.006 and 0.006 was obtained for TAME with methanol, 1-propanol and 1-pentanol, respectively.

Viscosity of liquid mixtures in terms of pure components was predicted using several nonlinear models of Hind, Auslander, Grunberg-Nissan and McAllister for binary mixtures of ETBE with 2-ethoxyethanol (EE), 2-(2-ethoxy-ethoxy)ethanol (DEE) and 2-[2-(2-ethoxyethoxy) ethoxy] ethanol (TEE) by Cwiklińska et al. (2007).

Hind (Hind et al., 1960):

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12}$$

Grunberg-Nissan (Gundberg and Nissan, 1949):

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2\ln(d)$$

Auslander (Auslander, 1964):

$$x_1[x_1 + B_{12}x_2(\eta - \eta_1)] + A_{21}x_2[B_{21}x_1 + x_2(\eta - \eta_2)] = 0$$

McAllister (McAllister, 1960):

$$\ln\nu = x_1^2\ln\nu_1 + 3x_1x_2\ln Z_{12} + 3x_1^2x_2\ln Z_{11} + x_2^2\ln\nu_2 - \ln(x_1 + x_2(M_1/M_2)) + 3x_1^2x_2\ln(2/3 + M_2/3M_1) + x_2^2\ln(M_2/M_1) + 3x_1x_2^2\ln(1/3 + 2M_2/3M_1).$$

From the prediction for viscosity deviation of the ETBE mixtures using different nonlinear models at temperature 298.15 K, they have concluded that the Auslander equation gives better prediction in comparison with the other nonlinear models.

Nonlinear models have not yet been widely used for predicting excess thermophysical properties of fuel oxygenate mixtures.

Table-1 below summarizes all the binary systems of ether and alcohol that are reviewed in this paper with additional information of their process conditions which were not discussed earlier.
### Table 1. Summary of Review on Ether and Alcohol Binary Systems.

<table>
<thead>
<tr>
<th>Ether</th>
<th>Alcohol</th>
<th>Temperature (K)</th>
<th>Pressure (Mpa)</th>
<th>Viscosity</th>
<th>Excess Molar Volume</th>
<th>Excess Molar Entropy</th>
<th>Model used for Data Correlation</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl tert-butyl ether (MTBE)</td>
<td>Methanol</td>
<td>298.15, 313.15, 323.15</td>
<td>0.1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>1. Redlich-Kister</td>
<td>Tusel-Lenger et al., 1991</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
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<td></td>
<td></td>
<td>Bianco et al., 1994; Letcher and Govender, 1997</td>
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<tr>
<td></td>
<td>Ethanol</td>
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<td></td>
<td></td>
<td>1. Redlich-Kister</td>
<td>Park and Dass, 1999</td>
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<td>1-Propanol</td>
<td>298.15</td>
<td>0.1</td>
<td>✓</td>
<td></td>
<td></td>
<td>1. Redlich-Kister</td>
<td>Tomura et al., 2001</td>
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<td></td>
<td>2-Propanol</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cerêheiro et al., 2002</td>
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<tr>
<td></td>
<td>methanol</td>
<td>298.15</td>
<td>0.1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>1. Redlich-Kister</td>
<td>Park et al., 2002</td>
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<td>298.15</td>
<td>0.1</td>
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<td></td>
<td>1. Morris</td>
<td>Mato et al., 2008; Mato et al., 2010</td>
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<td>1-Butanol</td>
<td>298.15</td>
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<td></td>
<td></td>
<td>1. Redlich-Kister</td>
<td>Haga and Torres, 2011</td>
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<td></td>
<td>Methanol</td>
<td>298.15</td>
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<td>Park and Oh, 1998</td>
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<td>298.15</td>
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<td>Gonzalez-Olmos and Iglesias, 2007</td>
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<td>Orlikowska et al., 2007</td>
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<tr>
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<td>298.15</td>
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<td>Tong et al., 1996</td>
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<td>Letcher and Govender, 1997</td>
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<td>1-Hexanol</td>
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<td>Ethyl tert-butyl ether (ETBE)</td>
<td>Methanol</td>
<td>298.15</td>
<td>0.1</td>
<td>✓</td>
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<td>1. Redlich-Kister</td>
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<td>1. Redlich-Kister</td>
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<td>Propanol</td>
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<td>1. Redlich-Kister</td>
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<td>Butanol</td>
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<td>1. Redlich-Kister</td>
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<tr>
<td>tert-amy-ethyl-methyl-ether (TAME)</td>
<td>Ethanol</td>
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<td>0.1</td>
<td>✓</td>
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<td>1. Redlich-Kister</td>
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<tr>
<td></td>
<td>Methanol</td>
<td>298.15</td>
<td>0.1</td>
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<tr>
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<td>✓</td>
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<tr>
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<tr>
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CONCLUSIONS
The research on excess thermophysical properties are important because they provide information about intermolecular attraction forces in a liquid mixture. Using binary mixtures of ether and alcohol is said to give better gasoline performance compared using ether or alcohol alone (Blanco et al., 1994) as fuel additive.

There is lack of data on ETBE and TAME binary mixtures with alcohol as compared to MTBE. MTBE is more widely investigated because of its excellent performance compared to other ethers. The price of MTBE is cheaper than other ethers and it is good octane enhancer. Other than that, it is also easy for transfer and blending of MTBE with gasoline. Another main factor is cost of ETBE and TAME which is relatively high compared to MTBE. It might be possible that ETBE and TAME can’t be studied widely due to lack of financial resources.

There are still scarcity of data for complete set of thermophysical properties for some mixtures. It is important to have the complete set of properties on systems studied especially for many chemical engineering calculations for process design and separation. New research should focus on filling the gaps in property measurements.

In future work, it is recommended that the researcher should carry more attention to thermophysical properties data for binary mixtures of ETBE and TAME since there are still scarcity of data for these binary mixtures. Other than that, the correlation of the excess thermophysical properties data using different nonlinear models are still scarce. There has not been much study done on comparison between different nonlinear models. All the previous study has only mainly used Redlich-Kister model for correlation of excess properties data. It is important that we compare with different nonlinear models to obtain a more accurate data on the excess properties. Accuracy of excess properties data is very important as these data are used in designing of many chemical processes such as separation processes. Hence, researchers can also venture into the aspect of nonlinear modelling of these thermophysical properties.

REFERENCES


[2] Blanco, S. T., Munoz Embid, J. and Otin, S. (1994). Excess volumes of (2, 2, 4-trimethylpentane + methanol or ethanol or propan-2-ol or di-1-methylethyl ether or 1, 1-dimethylethyl methyl ether) and of (methanol or ethanol or propan-2-ol + di-1-methylethyl ether or 1, 1-dimethylethyl methyl ether) at the temperature 298.15K. The Journal of Chemical Thermodynamics, 26, pp.23-28.


