Densities, Viscosities and Excess Properties of Binary Liquid Mixtures of Methyl Tert-Butyl Ether (MTBE) with N-Methylaniline (NMA) from 308.15-318.15 K at 0.1 MPa

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Abstract: Densities and viscosities of binary liquid mixtures of Methyl Tert-Butyl Ether (MTBE) with N-Methylaniline (NMA) at temperatures of 308.15, 313.15 and 318.15 K have been measured experimentally at atmospheric pressure over the entire range of composition. The densities and viscosities of MTBE and NMA binary mixture show a decreasing trend with the increase in MTBE composition at all temperatures. In addition, Jouyban-Acree equation has been used to predict the densities and viscosities where low standard deviations of 0.0025 and 0.0168 have been obtained. The excess molar volumes and viscosity deviation have been calculated and correlated with the Redlich-Kister equation where a good fit was obtained. Sigmoid shape of excess molar volumes has been obtained where negative excess molar volumes were obtained at high mole fraction of MTBE for all temperatures. Negative viscosity deviation has been obtained which showed the strength of chemical interaction in terms of hydrogen binding between unlike molecules.

Key words: Density, viscosity, excess molar volume, viscosity deviation, methyl tert-butyl ether, N-methylaniline, binary mixture

INTRODUCTION

The study of thermophysical properties of binary liquid mixtures is important in the analysis of engineering problems related to mass transfer, heat transfer and fluid flow (Cano-Gomez *et al*., 2015). The availability of the related data is essential in designing and solving many engineering problems such as process calculations, simulations and pipe design (Ramesh *et al*., 2014; Hoga and Torres, 2011). Usually, the density and viscosity of liquid and liquid mixtures are useful for understanding the behavior and nature of molecules (Hoga and Torres, 2011). In addition, the information of excess properties of binary liquid mixtures is also significant in order to study the intermolecular interactions between the components (Kumar and Jeevanandham, 2012; Hoga and Torres, 2011; Kinart and Kinart, 2000). Thus, the lack of thermodynamic data and molecular interactions for binary mixtures would lead to serious problems in phase behavior, molecular interactions, safety and economic considerations for chemical industries (Kinart and Kinart, 2000).

Usually, additives are used as blending agents for gasoline formulation in order to improve combustion and reduce the levels of soot as well as particulate emissions (Meng *et al*., 2008). Thus, research studies involving ethers and anilines as potential additives are actively performed. This is due to the fact that ethers as pure component or binary components with the combination of anilines is widely used due to its compatibility with gasoline and its ability to enhance the octane number, combustion improvement and emissions reduction (Hoga and Torres, 2011; Pandiyan *et al*., 2011; Saleh *et al*., 2001). Methyl Tert-Butyl Ether (MTBE) is one of the important blending agents for gasoline formulation (Han *et al*., 2013; Gomez-Marigliano *et al*., 2009). The main advantages of MTBE are good octane enhance and its capability to reduce exhaust emissions, particularly carbon monoxide (Gomez-Marigliano *et al*., 2009). Meanwhile, aniline is normally used for the manufacturing of chemical products such as the production of synthetic dyes, hydroquinone and drugs. Recently, the use of aniline compound such as N-Methylaniline (NMA) has been tested as fuel additives in gasoline direct injection engine (Nagano *et al*., 2017; Pandiyan *et al*., 2011).

Due to the importance of fuel additives, researchers have studied the various works of thermophysical properties. Densities and viscosities of binary mixtures MTBE with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol and 1-hexanol have been determined at temperatures from 293.15-308.15 K

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(Hoga and Torres, 2011). Excess thermodynamic properties of binary and ternary mixtures containing MTBE, n-heptane and methanol at a temperature of 313.15 K have been investigated by Segovia *et al*. (1999). Vapor-liquid equilibria and excess molar volumes of MTBE+C_3-C_4 alcohol systems at 298.15 K have been studied by Park *et al*. (2002). Densities, viscosities and refractive indices have been measured for binary mixtures of aromatic amines such as aniline and o-anisidine with 2-alkoxyethanols at 303.15 K (Kumar and Jeevanandham, 2012). Thermodynamic properties of seven binary liquid mixtures, namely, Dipropylene Glycol Dimethyl Ether (DPGDME)+ methanol, 1-propanol, 1-pentanol, 1-heptanol at 298.15 K and oxolane+aniline, NMA and N-Ethylaniline (NEA) from temperatures 303.15-321.15 K have been computed in the work of Sanguri *et al*. (2018). Oswal *et al*. (2010) reported the thermodynamic and acoustic properties of oxolane with aniline, NMA and NEA at 303.15, 313.15 and 323.15 K. Densities, viscosities and ultrasonic sound velocities of NMA with methyl isobutylketone, 3-pentanone and cycloalkanones were measured at 303.15 K (Gowrisankar *et al*., 2013). Saleh *et al*. (2001) measured the excess molar volume of 1-propanol with aniline, NMA and N, N-dimethylaniline from 294.15-323.15 K.

Based on our review, there has yet to be an attempt on studying the densities, viscosities and excess properties of binary mixture MTBE+NMA. Thus, the objective of this study is to measure the densities and viscosities at three different temperatures: 308.15, 313.15 and 318.15 K under atmospheric pressure for binary mixtures of MTBE with NMA. This mixture is selected due to the fact that MTBE is mainly used in the industry as oxygenate additives in gasoline for improving the octane quality and reducing pollutant emissions. Meanwhile, NMA is added into gasoline to avoid high gum level that can contribute to the increment of carbon deposits in engine parts. In addition, the excess molar volumes and viscosity deviations are calculated from density and viscosity measurement data in order to analyze the nature of interaction between the molecules of the mixtures.

MATERIALS AND METHODS

Methyl Tert-Butyl Ether (MTBE) and N-Methylaniline (NMA) were purchased from Merck. The purity of all the chemicals was >99% and they were used as received without further purification. The binary mixtures at varying compositions were prepared in terms of volume fraction. Before mixing the two liquids, the mass of the liquid volume is measured in an analytical electronic balance (Mettler ME203) with a precision of 1×10^{-3} g. Anton Paar DMA 4500 M Model was used for measuring the density for pure liquid and binary liquid. The oscillating U-tube sensor is equipped in the instrument and the investigated temperature was kept constant with the uncertainty of ±0.01 K at 0.1 MPa. Viscosity was measured using Anton Paar Viscometer SVM 3001 which can be operated in the viscosity ranging from 0.2-30,000 mm^2sec^{-1}. The standard uncertainties for the density and viscosity werecalculated using a propagation error formula (Hall *et al*., 1975).

RESULTS AND DISCUSSION

The densities and viscosities of MTBE and NMA pure components are shown in Table 1. The Average Absolute Precentage Deviations (AAPD) shown in Eq. 1 is used to determine the difference between the measured and experimental data of densities and viscosities.

$$\text{AAPD} = \frac{1}{n} \left\{ \sum \frac{\left| y_i^{exp} - y_i^{cal} \right|}{y_i^{exp}} \times 100 \right\} \qquad (1)$$

where, y_i^{exp} and y_i^{cal} are the experimental and literature densities and viscosities and n is the number of experimental data points. AAPD of 0.27 and 1.24% have been obtained for densities and viscosities measurements, respectively. This indicates that the densities and viscosities data of the pure components measured in this work are relatively in agreement with the values reported in the literature.

Table 1: Comparison of experimental densities and viscosities of pure components at different temperatures and literature values

Components	Temperature (K)	Density, ρ (gcm^{-3})		Viscosity, η (MPa.s)	
		Experimental	Literature	Experimental	Literature
MTBE	308.15	0.723	0.724[a] 0.726[b]	0.315	0.303[b]
	313.15	0.717	0.720[a] 0.722[b]	0.283	0.284[b]
	318.15	0.714	0.713[a] 0.718[b]	0.268	0.266[b]
NMA	308.15	0.975	0.974[c]	1.688	1.597[e]
	313.15	0.971	0.970[d] 0.970[c]	1.564	-
	318.15	0.966	0.966[c]	1.422	-

[a]Landaverde-Cortes *et al*. (2007), [c]Saleh *et al*. (2001), [d]Pandiyan *et al*. (2011), [e]Prasad and Ray (2008)

Table 2: Densities and viscosities at different temperatures and mole fractions for MTBE (1)+NMA (2)

	T = 308.15 K		T = 313.15 K		T = 318.15 K	
x_1 (mol mol^{-1})	ρ (gcm^{-3})	η (MPa.s)	ρ (gcm^{-3})	η (MPa.s)	ρ (gcm^{-3})	η (MPa.s)
0	0.975	1.688	0.971	1.564	0.966	1.422
0.086	0.959	1.491	0.951	1.359	0.947	1.237
0.186	0.932	1.242	0.924	1.136	0.919	1.074
0.276	0.909	1.080	0.899	0.994	0.895	0.951
0.379	0.888	0.911	0.880	0.862	0.875	0.814
0.480	0.864	0.814	0.852	0.743	0.848	0.679
0.577	0.839	0.681	0.835	0.642	0.831	0.557
0.688	0.806	0.550	0.804	0.525	0.799	0.432
0.790	0.781	0.422	0.772	0.423	0.764	0.342
0.903	0.754	0.349	0.749	0.331	0.744	0.303
1	0.723	0.315	0.717	0.283	0.714	0.268

Table 3: Coefficients of Jouyban-Acree Model for densities and viscosities prediction for MTBE+NMA binary mixture at different temperatures

Properties	Temperature (K)	J_0	J_1	J_2	σ
Densities	308.15	3.1225	0.4447	-1.0349	0.0019
	313.15	2.4696	2.4638	2.2167	0.0025
	318.15	4.4453	3.6103	1.2312	0.0003
Viscosities	308.15	9.5855	-1.9427	-24.3377	0.0168
	313.15	12.6631	12.8913	-12.6453	0.0084
	318.15	10.0853	-29.1367	-49.6668	0.0046

The density and viscosity results for binary mixture of MTBE with NMA at temperatures of 308.15, 313.15 and 318.15 K are shown in Table 2. Overall, the densities of MTBE+NMA binary mixture had decreased with an increase in the MTBE composition and temperature. In terms of viscosity, it was observed that the viscosities decreased with the respective increment of the temperature. The decrement trend in densities and viscosities of MTBE+NMA is due to the fact that as the mole fraction of MTBE is increased, its binding with anilines decreased, producing a flow that is less dense, lighter, less viscous and easy in flow.

The densities and viscosities of MTBE+NMA binary mixture have been correlated using the Jouyban-Acree Model as shown in Eq. 2:

$$\ln Q_{m,T} = f_1 \ln Q_{1,T} + f_2 \ln Q_{2,T} + f_1 f_2 \sum_{k=0}^{2} \left[\frac{J_k (f_1 - f_2)^k}{T} \right] \quad (2)$$

where, $Q_{m,T}$, $Q_{1,T}$ and $Q_{2,T}$ are the properties of the binary mixture, pure component 1 and pure component 2, respectively at the investigated temperature. f_1 and f_2 are the volume fractions of the pure components 1 and 2. J_k is the adjustable parameter for the given binary mixtures. The reliability of the model prediction is evaluated based on the standard deviations shown in Eq. 3:

$$\sigma = \left[\frac{\sum_{i=1}^{N} \left(y_i^{exp} - y_i^{cal} \right)^2}{N - n} \right]^{1/2} \quad (3)$$

where, N is the number of experimental data points and n is the order of the fitting polynomial. The estimated

coefficients using Jouyban-Acree Model for densities and viscosities prediction with their standard deviation are shown in Table 3. Based on the Jouyban-Acree Model, the standard deviation obtained for densities and viscosities prediction is <0.0025 and 0.0168, respectively. Low standard deviation indicates that the predicted coefficients of the Jouyban-Acree Model are able to accurately predict the densities and viscosities of MTBE+NMA at different temperatures.

Other than density and viscosity, the excess properties of the binary mixtures such as excess molar volumes and viscosity deviation also provide important information regarding the strength of the molecular interaction present in the mixtures. The excess molar Volume (V^E) of the binary liquid mixtures is calculated using the following equation:

$$V^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right) \quad (4)$$

where, M_1, M_2, ρ_1 and ρ_2 represent the molar masses and densities of components 1 and 2 and ρ is the density of the liquid mixture. The viscosity deviation ($\Delta\eta$) of the binary liquid mixture is defined by:

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (5)$$

where, η, η_1 and η_2 are the dynamic viscosity of binary liquid mixture, components 1 and 2, respectively. The calculated excess molar volumes and viscosity deviations for MTBE+NMA binary mixture at different temperatures are shown in Table 4. In addition, Redlich-Kister equation is used to predict the excess molar volumes and viscosity deviation as shown in Eq. 6:

Table 4: Excess molar volumes and viscosity deviations of MTBE+NMA binary mixture at temperatures of 308.15, 313.15 and 318.15 K

	T = 308.15 K		T = 313.15 K		T = 318.15 K	
x_1 (mol mol^{-1})	V^E (cm^3 mol^{-1})	$\Delta\eta$ (MPa.s)	V^E (cm^3 mol^{-1})	$\Delta\eta$ (MPa.s)	V^E (cm^3 smol^{-1})	$\Delta\eta$ (MPa.s)
0	0	0	0	0	0	0
0.086	0.58286	-0.09900	0.72313	-0.08491	0.88696	-0.07582
0.186	1.02900	-0.19130	1.21494	-0.17737	1.36512	-0.15393
0.276	1.00193	-0.22922	1.20131	-0.21660	1.28460	-0.19264
0.379	0.31608	-0.24723	0.46726	-0.23105	0.53970	-0.21113
0.480	-0.33348	-0.24468	-0.44079	-0.22786	-0.57582	-0.20884
0.577	-1.02801	-0.23207	-1.15087	-0.21713	-1.25872	-0.19939
0.688	-1.56151	-0.21376	-1.71822	-0.19903	-1.97889	-0.17637
0.790	-1.86364	-0.18158	-2.01505	-0.15924	-2.24366	-0.14755
0.903	-1.51569	-0.09904	-1.62516	-0.08613	-1.78428	-0.07682
1	0	0	0	0	0	0

Table 5: Coefficients of Redlich-Kister equation for excess molar volume and viscosity deviation of MTBE+NMA binary mixture at all temperatures

		Coefficients					
Properties	Temperature (K)	A_0	A_1	A_2	A_3	A_4	σ
Excess molar volume	308.15	-1.9599	14.8769	1.9876	0.8145	-10.1520	0.0077
	313.15	-2.3191	16.4136	6.0479	1.3039	-14.8516	0.0075
	318.15	-2.3764	18.5360	3.2203	1.6118	-10.2361	0.0094
Viscosity deviation	308.15	-0.9035	-0.4048	-0.7896	0.6364	0.8970	0.0023
	313.15	-0.7766	-0.4613	-0.6518	0.2770	0.5385	0.0006
	318.15	-0.7682	0.3191	-0.4744	-0.6697	0.2487	0.0005

$$Y_m = x_1 x_2 \sum_{i=0}^{i=n} A_i \left(x_2 - x_1\right)^i \quad (6)$$

where, A_i are adjustable parameters that can be fitted with the experimental results using the least-squares regression method. The coefficients of Redlich-Kister equation for excess molar volumes and viscosity deviation at all temperatures are shown in Table 5, along with the standard deviation (σ). Low standard deviations have been obtained for excess molar volume and viscosity deviation, indicating a reliable prediction has been obtained.

Figure 1 and 2 show the behavior of excess molar volume and viscosity deviation at all temperatures for MTBE+NMA binary mixture. Based on Fig. 1 and 2, it is clearly shown that the excess molar volume and viscosity deviation were successfully fitted using the estimated adjustable coefficients for Redlich-Kister equation. For excess molar volume, it can be seen that the sigmoid curves have been obtained for MTBE+NMA binary mixture as shown in Fig. 1. The excess molar volumes are positive at low mole fractions of MTBE while it became negative when the mole fraction of the binary mixture is more than 0.44. Both positive and negative values were observed to increase with an increase in temperature over the entire composition. At low mole fraction of MTBE, positive excess molar volumes are obtained due to the expected dispersive interaction force between the unlike two molecules (Hoga and Torres, 2011). Since, only a single methyl group is attached to atom N in the NMA component, it can be suggested that less extensive associated of methyl group through H-bonding is expected due to the more steric hindrance by the methyl group that is attached to the NMA. However in the MTBE rich region, negative
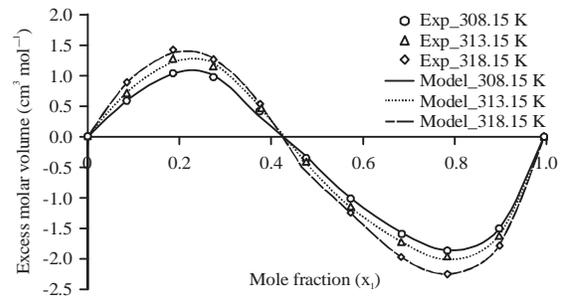

Fig. 1: Excess molar volumes for MTBE+NMA binary mixture for all temperatures
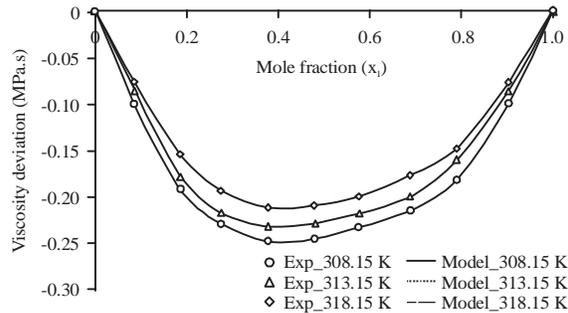

Fig. 2: Viscosity deviations for MTBE+NMA binary mixture for all temperatures

excess molar volumes are obtained. This may be attributed to the strong specific or chemical interactions between MTBE and NMA. As the composition of the MTBE increased, the molar volumes of MTBE also increased in which the MTBE becomes superior to NMA. Consequently, the mixture containing ether and aniline

group for MTBE+NMA will associate with the hydrogen bonding due to structural effects. Thus, a more efficient packing and attractive interaction takes place when MTBE and NMA aremixed, leading to the negative excess molar volume. In terms of viscosity deviations, negative values are obtained for MTBE+NMA for all temperatures but they become less negative with an increase in temperatures from 308.15, 313.15 and 318.15 K as shown in Fig. 2. The viscosity of the liquid mixture is usually determined by many factors which may include the structure of the molecules, effectiveness of the intermolecular binding forces and thermal energy (Oswal *et al.*, 2010). Dubey and Kumar (2016) stated that in addition to the intermolecular interaction, the shape and size of the molecules may also influence the value-sign and range of the viscosity deviation. They have also found that the negative deviation observed at entire composition range may be attributed to the strength of chemical or specific interaction such as hydrogen binding between the unlike molecules. Thus, it can be concluded that the negative deviations for MTBE+NMA binary mixture indicate the inclusion of small molecules of NMA in the structure of larger molecules such as MTBE. This suggests the breaking up of the self-associated aniline group in NMA components into MTBE molecules.

CONCLUSION

In this study, the densities and viscosities of MTBE+NMA are measured experimentally at temperatures between 308.15 and 318.15 K. As the MTBE composition is increased, the densities and viscosities of MTBE+NMA decreased at all temperatures. Jouyban-Acree Model is used to predict the densities and viscosities where a good agreement has been obtained between the experimental and prediction values. Meanwhile, the Redlich-Kister equation is used for predicting excess molar volumes and viscosity deviation where low standard deviations of 0.0094 and 0.0023 were obtained, indicating a well-fitted predictive model. In terms of the trends, the excess molar volumes at all temperatures for MTBE+NMA have changed from positive to negative values when the MTBE composition is increased. This indicates the strength of interaction between the unlike molecules obtained. The negative viscosity deviation is obtained for the MTBE+NMA binary mixture which indicates the inclusion of small molecules of NMA into MTBE molecules.

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