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Densities and viscosities for binary mixtures of polyoxymethylene dimethyl ethers with different CH_2O chain length n = 2, 3, 4 at different temperatures

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ABSTRACT

Experimental densities and viscosities for the binary mixtures of polyoxymethylene dimethyl ethers with different CH_2O chain length n = 2, 3, 4 were measured over a temperature range of 288.15 K–313.15 K and at the atmospheric pressure of 0.1 MPa. It is found that the order of densities and viscosities for pure components is $PODE_2$ < $PODE_3$ < $PODE_4$ at the same temperature. Meanwhile, for binary mixtures ($PODE_2$-$PODE_3$, $PODE_2$-$PODE_4$, $PODE_3$-$PODE_4$), the densities and viscosities decreased with the increase of mole fraction of light component. On the basis of experimental data, the excess molar volumes and the viscosity deviations for the binary mixtures were calculated and correlated by the Redlich-Kister equation, while the excess Gibbs energy of activation for binary mixtures ($PODE_2$-$PODE_3$, $PODE_2$-$PODE_4$, $PODE_3$-$PODE_4$) were also calculated and correlated. The results indicated that the difference of the CH_2O chain length has a significant influence on the densities and viscosities of binary mixtures of polyoxymethylene dimethyl ethers.

1. Introduction

Polyoxymethylene dimethyl ethers ($PODE_n$) are a series of polymer of the monomer formaldehyde (CH_2O), which the chemical structure is $CH_3O(CH_2O)_nCH_3$ (n is the chain length of CH_2O groups, generally from 2 to 8) [1,2]. Polyoxymethylene dimethyl ethers with different chain length of CH_2O groups of n = 2–8, were labeled as $PODE_2$ ($C_4H_{10}O_3$, IUPAC Name: methoxy(methoxymethoxy)methane), $PODE_3$ ($C_5H_{12}O_4$, IUPAC Name: 2,4,6,8-tetraoxanonane), $PODE_4$ ($C_6H_{14}O_5$, IUPAC Name: 2,4,6,8,10-pentaoxaundecane), etc (Fig. 1), respectively. These compounds with higher oxygen content and cetane number, lower cold filter plugging point and solidification point, are environmentally friendly due to their extremely few sulfur content and zero arene content [3,4]. $PODE_n$ is being recognized as promising blending components for diesel without changing the structure of diesel engine, which can improve the combustibility of diesel, enhance the efficiency of combustion, and reduce the emissions of NO_x, PM, CO_x and soot [5,6].

$PODE_n$ can be produced from methanol and its downstream, through the reaction of component A and B over solid acid catalysts, with potential scientific values and application prospects for methanol and coal chemical industry. Here, component A refers to the compounds (trioxane, paraformaldehyde, or formaldehyde) providing the monomer formaldehyde (CH_2O), while component B refers to the compounds (methanol or dimethoxymethane) providing end-group (CH_3 or CH_3O) [7,8].

It is reported that the synthesis of $PODE_n$ followed the sequential propagation mechanism, which obeyed the Schulz-Flory distribution [9,10]. Among the $PODE_n$ homologues (n = 2–8), the components of $n \geq 5$ have some shortcomings such as poor low-temperature fluidity, higher melting points, and higher viscosities, so that the components of n = 3 and n = 4 were chosen as the target compounds matching with diesel. However, densities of the $PODE_{3-4}$ were higher than conventional diesel [7], which can be decreased by adding small amounts of $PODE_2$ to meet the conventional diesel [11].

Generally, density and viscosity are the key parameters for diesel engine, which affect the start of injection, the injection pressure

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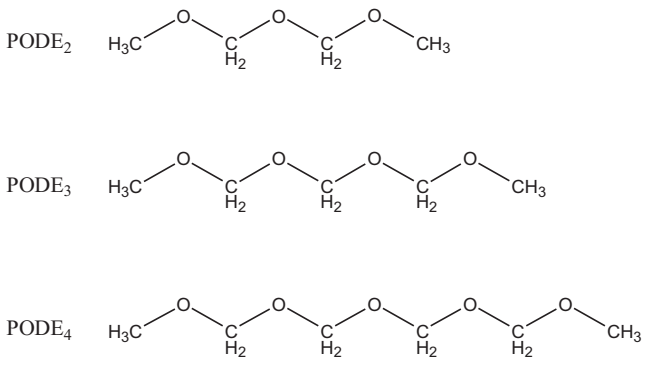

Fig. 1. Chemical structures of $PODE_2$, $PODE_3$, and $PODE_4$.

and the fuel spray characteristic, and further influence the engine performance, combustion and exhaust emissions [12,13]. Therefore, the knowledge of fundamental physicochemical properties is extremely important to optimize the composition of $PODE_n$ as blending components for diesel. However, there are few studies about the density and viscosity of $PODE_2$, $PODE_3$, $PODE_4$, and its binary mixtures.

In this work, the densities and viscosities for pure components ($PODE_2$, $PODE_3$, $PODE_4$) and binary mixtures ($PODE_2$-$PODE_3$, $PODE_2$-$PODE_4$, $PODE_3$-$PODE_4$) were measured over a temperature range of 288.15 K–313.15 K at 0.1 MPa, and correlated by empirical equations. Furthermore, the excess molar volumes (V^E) and the viscosity deviations ($\Delta\eta$) for binary mixtures were calculated and correlated by the Redlich-Kister equation. Additionally, the excess Gibbs energy of activation (ΔG^{*E}) for binary mixtures ($PODE_2$-$PODE_3$, $PODE_2$-$PODE_4$, $PODE_3$-$PODE_4$) were also calculated and correlated on the basis of experimental data.

2. Experimental sections

2.1. Materials

Ethanol was purchased from Tianjin guangfu chemical reagent Co. with mass fraction purity higher than 99%. $PODE_2$, $PODE_3$ and $PODE_4$ were prepared in laboratory according to the literature [14,15]. The pure $PODE_2$, $PODE_3$ and $PODE_4$ were exactly distilled twice after being preliminarily separation, respectively. The purity of different components were analyzed by the gas chromatograph (Agilent 7820A) equipped with a SE-54 capillary column (60 m × 0.25 mm × 0.25 μm) connected to a FID. Meanwhile, acetone and octane were used as solvent and the internal standard, respectively [15]. Detailed information on the materials was shown in Table 1. It can be seen that the mass fraction of water content in $PODE_2$, $PODE_3$ and $PODE_4$ were all lower than 0.001, hence, the trace amount of water did not have negative effect on the properties of pure components.

2.2. Density and viscosity measurements

All the binary mixtures were prepared by using an analytical balance (Mettler Toledo, AL204, Switzerland) with a precision of 0.0001 g. The uncertainty of mole fraction (x_1) is determined as u (x_1) = 0.01. Density (ρ) measurements were performed using a densitometer (METTLER TOLEDO, Densito 30PX, Switzerland), while viscosity (η) measurements were performed by a rotary viscosimeter (SHANGHAI SUNNY HENGPING SCIENTIFIC INSTRUMENT CO.,LTD, NDJ-5S, China) under the same conditions with density measurements (Fig. 2). The experiments were carried out over temperature range of 288.15 K to 313.15 K at 0.1 MPa with uncertainty $u(T)$ = 0.01 K and $u(p)$ = 0.005 MPa.

The densitometer and viscosimeter were calibrated at 298.15 K with pure water (ρ = 0.99705 g cm^{-3}, η = 0.89008 mPa s) and ethanol (ρ = 0.78547 g cm^{-3}, η = 1.0849 mPa s) before the measurements, the reference data were obtained by using REFPROP software. The comparison of experimental values with literature values [16–18] of densities and viscosities for pure components ($PODE_2$, $PODE_3$ and $PODE_4$) at 298.15 K and 0.1 MPa were given in Table 2. It can be seen that the experimental values of densities for $PODE_3$ and $PODE_4$ were close to the literature values, while the densities of $PODE_2$ were slightly above literature values. The experimental density of $PODE_2$ (0.9901 g cm^{-3}) was higher than the literature values. In order to verify the experimental value, two instruments were used to measure the density of $PODE_2$ at 298.15 K and 0.1 MPa. The results showed that the density measured by the densitometer (METTLER TOLEDO, Densito 30PX, Switzerland) was 0.9899 g cm^{-3}, while the density measured by the electronic density balance (Shanghai Yueping scientific instrument Co., Ltd., JA2003 J, China) was 0.9892 g cm^{-3}. The difference between experimental values and literature values may be resulted from the cumulative errors of the operation of instrument, the precision of temperature control, ambient pressure and the purity of components.

At each composition and temperature, the measurements were repeated three times, and the average values were used to calculate the density and viscosity.

3. Results and discussion

3.1. Density

Densities of pure components ($PODE_2$, $PODE_3$, $PODE_4$) and binary mixtures ($PODE_2$-$PODE_3$, $PODE_2$-$PODE_4$, $PODE_3$-$PODE_4$) as function of mole fraction over temperature range of 288.15 K to 313.15 K at 0.1 MPa were graphically shown in Fig. 3 with the

Table 1
Description of materials used in this article.

Chemical Name	Source	Initial Mass Fraction Purity	Purification Method	Final Mass Fraction Purity[a]	Analysis Method[b]	Mass Fraction of Water Content[c]
Ethanol	Tianjin Guangfu Chemical Reagent Co.	0.995	None	NA	None	≤0.005
$PODE_2$	Prepared in laboratory	0.946	Distillation	0.995	GC	≤0.001
$PODE_3$	Prepared in laboratory	0.923	Distillation	0.995	GC	≤0.001
$PODE_4$	Prepared in laboratory	0.976	Distillation	0.995	GC	≤0.001

[a] NA = not applicable.
[b] GC = gas chromatography [15].
[c] Water content was determined by Karl Fischer titration.