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Experimental investigations for the phase equilibrium of R1234yf and R1234ze(E) with two linear chained pentaerythritol esters

Xiaopo Wang *, Yanjun Sun, Na Gong

Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, People's Republic of China

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ABSTRACT

R1234yf and R1234ze(E) have been proposed as the most promising refrigerants to substitute R134a due to its low global warming potential. Experimental measurement for the phase equilibrium of R1234yf (or R1234ze(E)) and lubricant oil is an important task in the practical refrigeration system. In this work, the solubilities of R1234yf in pentaerythritol tetrabutyrate (PEC4) and in pentaerythritol tetrapentanoate (PEC5), the two linear chained precursors of polyol ester lubricants, have been measured from $T = (293.15$ to $348.15)$ K based on the isochoric method. The obtained solubility data were compared with the literature results of R1234ze(E) and R134a in PEC5. In addition, the solubility of R1234ze(E) in PEC4 was also reported from $T = (293.15$ to $353.15)$ K for further comparison. The experimental solubility data were correlated using the Peng–Robinson equation of state with HVOS mixing rules and Wilson equation for the excess Gibbs energy at infinite pressure.

1. Introduction

According to the Montreal Protocol, hydrofluorocarbons (HFCs) were developed as alternative to substitute CFCs and HCFCs and have been extensively used in refrigeration and air conditioning vapor compression systems over the last 20 years. However, due to the high global warming potential (GWP), HFCs were considered as greenhouse gases under the Kyoto Protocol in 1997. Moreover, the European Union's F-gas Regulations and the MAC (mobile air-conditioning system) Directive bans the use of F-gases with a GWP higher than 150 in new models and new vehicles starting from January 1, 2011 and January 1, 2017, respectively. To search alternative refrigerants for high GWP refrigerant replacement become a major issue for the refrigeration industry.

In recent years, hydrofluoroolefins (HFOs) were identified as promising "next generation" refrigerants with lower GWPs than HFCs [1,2]. Among the HFOs, 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) and *trans*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(E)), developed by Honeywell and DuPont, were the most acceptable alternatives. Both refrigerants are low flammable, present low toxicity levels, with zero ODP and very low GWP. Especially for R1234yf, due to its similar thermodynamic properties with R134a, it can, in principle, be considered as a "drop-in" solution to replace R134a in mobile air conditioning systems and other applications of refrigeration and air conditioning [3].

It is well known that the knowledge of the phase behavior of (refrigerant + lubricant oil) mixtures is a key factor for the performance and reliability of the compressed refrigeration system. To our best knowledge, there is still a lack of experimental data in the open literature on the phase behavior of (R1234yf (or R1234ze(E)) + lubricant) mixtures. Bobbo et al. [4] reported solubility data of R1234yf in two commercial PAG oils. Marcelino Neto et al. [5] measured the phase equilibrium of the R1234yf/POE ISO VG10 mixture, and compared the results with R134a/POE ISO VG10 under the same conditions. However, the effective composition and the constituent proportion in PAG or POE lubricants are not available in the literature. It is therefore difficult to describe the phase behavior using the general thermodynamic models, and the models cannot be used to other mixtures which have not yet been measured.

For the POE oil, the main components are pentaerythritol esters, which can be linear chained, branched chained, and cyclic chained esters [6]. Figure 1 shows the chemical structure of different linear chained esters. Recent years, to study the solubility of refrigerant in those pentaerythritol esters have attracted more attention. Wahlstrom and Vamling [7,8] reported the solubilities of different HFCs, such as HFC134a, HFC152a, HFC32, HFC125, and HFC143a, in PEC5 and PEC9. Bobbo [9], Fandino [10–12], Fedele [13], and Pernechele [14] investigated the solubility of carbon dioxide in linear chained esters (PEC4–PEC9). They also measured the solubility

* Corresponding author. Fax: +86 29 82668789.
E-mail address: wangxp@mail.xjtu.edu.cn (X. Wang).

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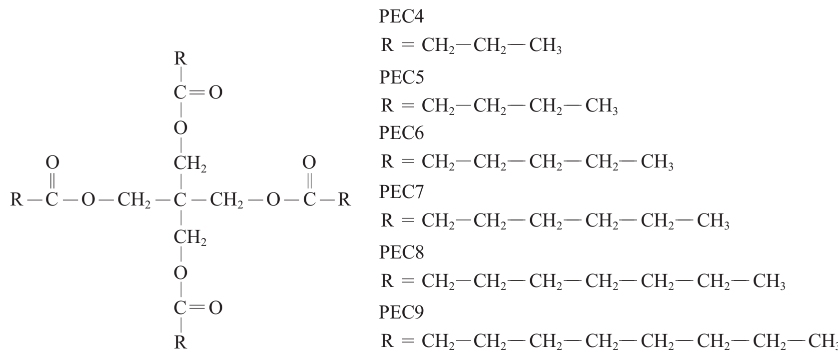

FIGURE 1. Chemical structure of different PECs.

data of carbon dioxide in branched chained and cyclic chained esters [10,15,16]. Those measurements are very valuable in the evaluation and development process of a predictive model [17]. Previous studies of our group about the solubility of R1234ze(E) in pentaerythritol tetrapentanoate (PEC5) have been reported [18]. In this work, the solubilities of R1234yf in pentaerythritol tetrabutyrate (PEC4) and pentaerythritol tetrapentanoate (PEC5), and R1234ze(E) in pentaerythritol tetrabutyrate (PEC4) were investigated. The experimental results were modeled with the Peng–Robinson equation of state and HVOS mixing rules.

2. Experimental section

2.1. Materials

R1234yf ($CFCF_3{=}CH_2$; CAS No. 754-12-1) and R1234ze(E) ($CF_3CH{=}CHF$; CAS No. 29118-24-9) were supplied by Honeywell with declared mass purity of 99.9%. Before experiment, the sample was purified several times by using freeze–pump-thaw cycles with liquid nitrogen and a high vacuum pump to eliminate the presence of any remaining non-condensable gases.

PEC4 ($C_{21}H_{36}O_8$, CAS No. 7299-98-1) and PEC5 ($C_{25}H_{44}O_8$, CAS No. 15834-04-5) were synthesized by Chemipan (Poland) on a laboratory scale with a declared purity higher than (98 and 99)%, respectively. It was used with no further purification. The chemical formula of PEC4 and PEC5 is $C(CH_2OCOCH_2CH_2CH_3)_4$ and $C(CH_2OCOCH_2CH_2CH_2CH_3)_4$, respectively. Table 1 shows the summary of the sample descriptions used in the present work.

2.2. Apparatus and method

The solubility measurement was performed with an isochoric apparatus which has already been extensively described in our previous papers [18]. Here only its main characteristics are illustrated. Figure 2 shows the schematic diagram of the solubility measurement system.

The experimental equipment consists of two different volume stainless steel cells, named equilibrium cell with a calibrated volume of 31.33 cm^3 and gas cell with a calibrated volume of 73.26 cm^3, respectively. The two cells were immersed in liquid thermostatic bath (Fluke 7008) with a stability of lower than 0.01 K. A 100 Ω platinum resistance thermometer, supplied by Fluke and calibrated by National Institute of Metrology of China, was used to measure temperature with an accuracy of about 0.02 K. The combined expanded uncertainty of the temperature measurement was 0.03 K with a level of confidence of 0.95

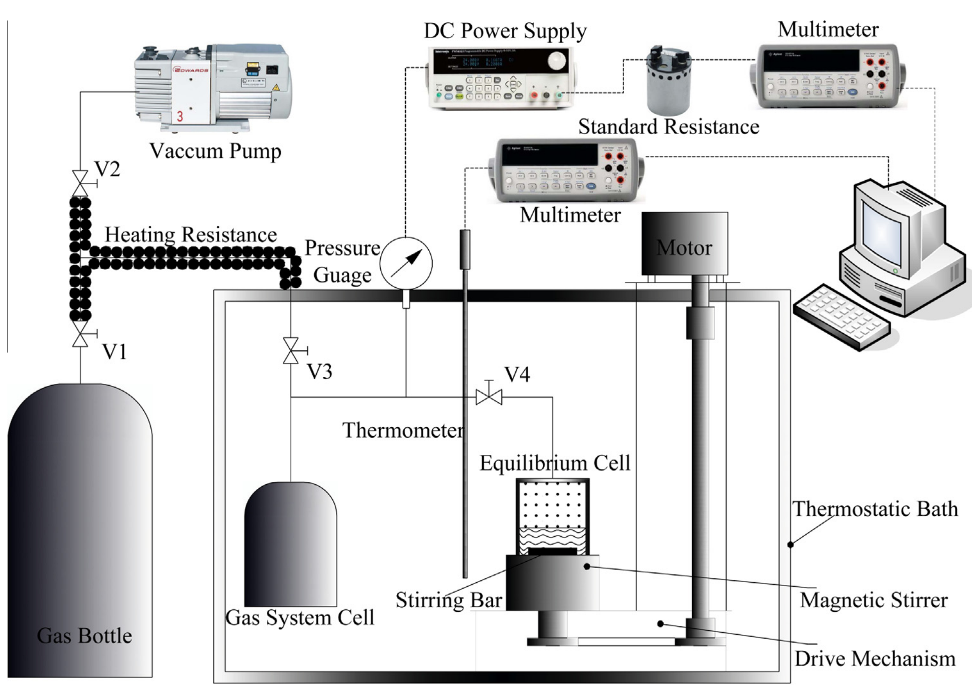

FIGURE 2. Schematic diagram of the solubility measurement system.