Research on the miscibility of R1234ze(E)/RE170 with mineral oil

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Abstract

R1234ze (E) has become the focus of refrigeration industry as a new generation of environmental protection refrigerants. Lubricating oil is indispensable in vapor compression refrigeration cycle. So, seeking the appropriate lubricating oil, which has excellent thermodynamic property during blending with the specific refrigerant in the system, became an important research under the background of energy conservation and environment protection. In this paper, a new experiment system was designed and built based on the operating standards named SH/T 0699 and JIS K2211 with the associated consideration. Then, the critical miscibility temperature (T_{CST}) data of different mass fraction of R1234ze(E)/RE170 with a 3GS naphthenic mineral oil were measured and analyzed at a temperature ranging from -50℃ to 40℃. Several typical statuses and micro-phenomenon of the solutions blended by refrigerants and mineral lubricants were presented as well. The results showed that the miscibility of R1234ze(E)/RE170 mixed solution with mineral oil was mainly affected by the content of RE170 when the mass fraction of mineral oil was 14.4% ± 0.8%. It found that if the content of R1234ze(E) was more than 60%, the critical miscibility temperature of R1234ze(E)/RE170 with mineral oil will rise rapidly.

Keywords: miscibility, experiment, R1234ze(E)/RE170

Introduction

The invention of refrigerants changed the lifestyle of human beings. But drawbacks were also gradually display with refrigerants system used widely. For the sake of protect the earth's ozone layer from emission of destructive chemicals, governments adopted the Montreal protocol to eliminate the Chlorofluorocarbons (CFCs) refrigerants in 1987. The greenhouse effect promoted the legislation of Kyoto Protocol in 1997, and the refrigerants with high Global Warming Potential (GWP) were banned. Nowadays, CFCs had been phased out by 2010 and hydrochlorofluorocarbons (HCFCs) and high GWP HydroFluoroCarbons (HFCs) are going to phase out by 2040. Consequently, Hydrofluoroolefins(HFOs), natural refrigerants and low GWP HFCs has been proposed as alternative refrigerants.

Focusing on HFO, increased attention has been taken on 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) and trans-1,3,3,3-tetrafluoropropene (R1234ze(E)) because of their low GWP. In recent year, R1234yf and R1234ze(E) prevail as the most acceptable alternatives for HFCs. R1234yf has already been applied as alternative of R134a for mobile air conditioners and R1234ze(E) is being produced as a cover gas. Specifically, R1234ze(E) which offers a remarkably low GWP of four [1] relative to CO_2 for a 100 year time horizon were tested on thermodynamic and thermophysical properties by many researchers[2]. It was found that R1234ze(E) is low-flammable and present low toxicity levels, with no ODP and very low GWP.

Thermophysical properties of R1234ze(E) and its blends had been studied by many scholars. An amount of relevant experiment data of the thermophysical properties of R1234ze(E) were available in the open literature, which including density [3], viscosity [4], critical parameters [5], pρT properties [6], flammability [7], etc. Group contribution methods are used to predict the critical temperatures, critical pressures, critical densities, acentric factors, and ideal gas specific heats at constant pressure for eight fluorinated olefins, which included R1234ze(E)[8]. Hossain et al. [9,10] experimentally studied the condensation heat transfer and pressure drop in horizontal smooth tube of internal diameter 4.35 mm for R1234ze(E), R32 and R410A and found that heat transfer coefficients of R1234ze(E) are about 30% lower than R32 and about 28% higher than 410A.

In order to popularize R1234ze(E) to high-temperature heat pump systems, thermodynamic, experimental, and numerical assessments were presented [11].It was found that pure R1234ze(E) is not suitable for an alternative of R410A, but mixtures of R1234ze(E) and R32 are promising candidates for replacing R410A in domestic heat pump systems[12]. Van Long Le et al. [13] presents the system efficiency optimization scenarios of basic and regenerative supercritical organic Rankine cycles using R1234ze(E). Besides, the dynamic behavior of R1234ze(E) in adsorption cooling cycle powered by process waste heat or waste heat from automobile engine was investigated[14].

The miscible properties of refrigerants are indispensable for optimum design of energy-conversion systems and selection of the refrigerant. However, to the author's knowledge, only a limited number of the miscibility of R1234ze(E) and its blends could be found in the published literature. Therefore, this paper wishes to provide experiments and estimates of the miscibility of R1234ze(E)/RE170 with mineral oil.

2. Experimental

2.1. Materials

R1234ze(E) (Trans-1, 3, 3, 3-tetrafluoroprop-1-ene , CAS No. 1645-83-6)) was supplied by Honeywell with declared mass purity of 99.9%. RE170 (dimethyl ether, CAS Registry No. 115-10-6) was provided by Zhejiang Lantian Environmental Protection Co. Ltd. (FLTCO) with a mass fraction purity of > 0.9996. The mineral oil (3GS) used in the experiment was gained from Japan Sun Oil Co. Ltd. (SUNOCO). Table 1 shows the sample descriptions used in the present work, and the typical properties of the SUNOCO 3GS are shown in Table2. All materials were used without any further purification.

Table1. Description of Sample Used

Chemical name	formula	Mass fraction purity	source	CAS Registry No.
Trans-1, 3, 3, 3-tetrafluoroprop-1-ene	$C_3H_2F_4$	>0.999	Honeywell	1645-83-6
dimethyl ether	C_2H_6O	> 0.9996	FLTCO	115-10-6

Table 2. Typical Properties of the SUNOCO 3GS

Property	test method	3GS
Density/g•cm^{-3}（15℃）	ASTM D 1250	0.909

Color (ASTM)	ASTM D 1500	L0.5
Viscosity/mm2•s-1（40℃/100℃）	ASTM D 445	29.5/4.31
Aniline Point/℃	ASTM D 611	75.4
Flash Point / COC℃	ASTM D 92	178
Pour Point /℃	ASTM D 97	-40
Floc Point /℃	ANSI/ASHRAE 86	-53
Total Acidity/mg KOH/g	ASTM D 974	0.01

2.1. Experimental Apparatus and Procedure

Based on the reference standard SH/T 0699-2000 the People's Republic of China petroleum and chemical industry and Japan industrial standard JIS K2211-2009, we designed and built experiment system to investigate the miscibility of refrigerant with lubricant, as shown in figure 1. It mainly consists of four parts:

Part 1 is constant temperature system. Actually, it main consists of a thermostat which adopts a cascade refrigeration units. And the refrigerant of the low temperature side is R23 and high temperature side is R404A. The thermostatic bath is equipped with a automatic heating device, and precision platinum resistance temperature sensor (German Docorom company production of TR/02022 type sensor). The temperature of thermostatic bath ranges from -70℃ to 200℃, the temperature fluctuation is 0.5℃.

Part 2 is gas distributing system. Distribution system includes pressure sensor, electromagnetic valve, filter drier, vacuum device, buffer and electronic scale, etc. The whole system is connected with stainless steel pipe, and a dryer is set among the pipe to remove moisture in the system. In addition, we also use the vacuum pump for clean the system pipe.

Part 3 is equilibrium cell system. Including tube, stainless steel flange, platinum resistance thermometer. Test tube is a transparent quartz glass tube, a convex platform is put in its upper end. Between 2 pieces of homemade stainless steel flange, six brass bolt flange compression are put in vitro convex platform, so as to achieve the aim of tube top sealing. The temperature of the mixture measured directly by the insertion of the thermocouple. Platinum resistance thermometer has been the use of secondary standard platinum resistance to add digital voltage meter calibration with the accuracy of 0.15 K.

Part 4 is gas distributing system. The system mainly includes personal computer, Germany's Siemens programmable controller (PLC S7-200), temperature and pressure analog/digital quantity input/output module, the intermediate relay, ac contactor, etc. Using the control system to complete the test variable control, process monitoring, and the test data acquisition, realize the high precision automatic control of the test.

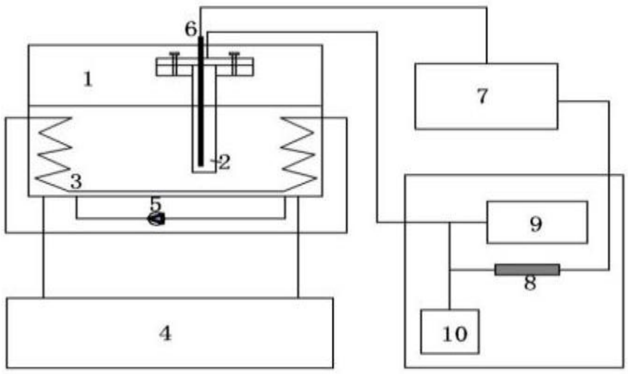


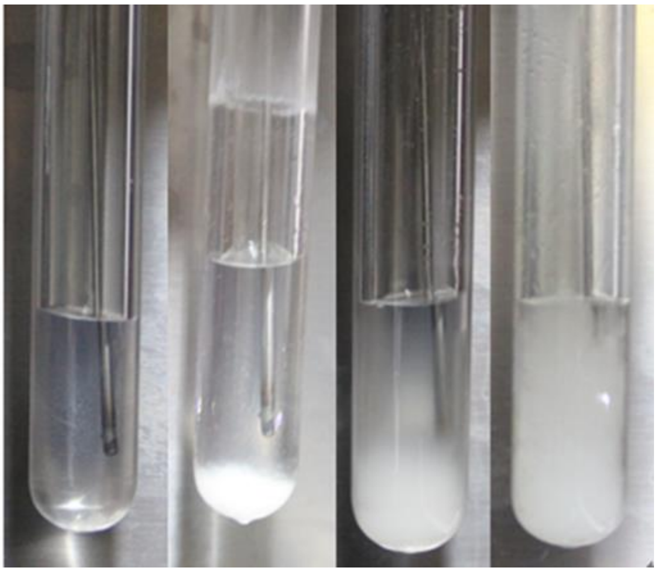
Figure 1. Schematic diagram of the experimental apparatus. 1, thermostatic bath; 2, equilibrium cell; 3, heater; 4, cascade refrigeration system; 5, circulation pump; 6, platinum resistance thermometer; 7, data collecting system; 8, pressure sensor; 9, vacuum pump; 10, sample

Before beginning the test, the whole experimental system will be clean and vacuum to 200 Pa. Then the test mixture solution (refrigerants and lubricating oil) was put into the test tube. The lubricating oil will be injected into the test cell by syringe at first. The test refrigerants fill into the cell by gas distributing system. After finishing the distribution of refrigerants and lubricating oil, the test tube was immersed in a thermostatic bath, the adjustable temperature system of thermostatic bath was range from 223.15 K to 343.15, which cooled by a cascade refrigeration system and heated by an electrical heater. The temperature data of platinum resistance thermometer was collected by programmable logic controller (PLC) and controlling systems were operated by a logic controller (PLC) and controlling systems were operated by an upper computer. Observing the state of mixed solution in the cell until two phase (a liquid layer formation, cloudiness, flocs or precipitate formation) appeared, when the temperature of thermostatic bath was changed from 223.15K to 343.15K. Then the cell should be agitated until previous signs disappeared and the temperature of thermostatic bath should also be readjusted so that the specific signs appeared again. At last, the temperature of the mixing solution was recorded as the T_{CMT} for that concentration as the two phase appeared again. Changing the concentration of refrigerants and lubricating oil, the above procedures were conducted repeatedly.

3. Results and Discussion

RE170 (DME), also called dimethyl ether, can be obtained by natural gas conversion. The ODP and GWP value of RE170 is 0, which has excellent environmental performance. Through the study found that the saturation vapor pressure curve is slightly lower than R134a, while it is higher than that of R600a. So RE170 can be used as perfusion alternative in R600a and R134a refrigerators. In the refrigerator, under the condition of the theoretical calculation of the COP of 6.2% percentage points higher than R600a .In addition, RE170 can also be used in the high temperature heat pump to replace R134a, and improved the COP of system. RE170, therefore, is a kind of new environmental protection refrigerant. Based on our previous test research shows that RE170 with mineral oil solution in the range of 10% to 60%, oil content temperature range for - 50℃ and 40℃, the mixed solution are presented for uniform transparent state. Therefore RE170 is very suitable as a component in green refrigerant or mixed refrigerants.

In order to explore the miscibility characteristics of mixed refrigerants(mineral oil and R1234ze (E)), we conducted the miscibility experiment on R1234ze(E)/RE170 + mineral oil . The mass fraction of mineral oil in R1234ze (E)/RE170 mixed refrigerant solution was 14.4% ± 0.8%, the mass fraction R1234ze (E) was 31%~70%, temperature was ranged for−55~35℃.The results were shown in figure 2 and table 3.



a b c d

Figure 2 a, mineral oil and refrigerant mixture solutions of homogenous solution; b, a small amount of floc; c, d, a large number of floc stratification.

Table 3 Miscibility experiment data of R1234ze(E)/RE170 + mineral oil

Mass fraction of R1234ze(E)/%	Mass fraction of oil/%	T_{CST}/℃
69.23	14.82	31.5
66.99	14.41	22.5
64.94	14.03	14
63.14	13.70	8
59.96	15.03	-3
56.48	15.55	-11
56.94	13.79	-4
55.74	14.12	-13
53.40	13.71	-16
49.04	14.80	-23.5
45.88	13.77	-27
42.05	14.61	-37
39.77	13.80	-45
31.17	15.47	-51

After completing the injection of mixed refrigerant and mineral oil, the mixed solution is soluble, rendering and uniform and transparent solution, as shown in figure 2a. When the reduction of temperature by cryogenic tank by an observe windows found a small amount of floc settling at the bottom of the tube, as shown in figure 2b. Continue to maintain the temperature or continuous cooling, we found a large number of floc generated in the bottom of the test tube , which resulted in mixed solution into ivory, as shown in figure 3c. If the temperature continues to decrease produces, a layered phenomenon will be observed, which was that the tube is clear at the bottom of tube and the surface appear thin oil layer, as shown in figure 3d. The results showed that when R1234ze (E) of mixed refrigerant mass fraction is 30% - 70%, as increasing the content of R1234ze(E), the critical miscibility temperature will rise rapidly, as shown in figure 3. Its change rule in measuring temperature range is very obviously, the mixture of the critical miscibility temperature of R1234ze (E) content of corresponding relation is shown in the following formula:

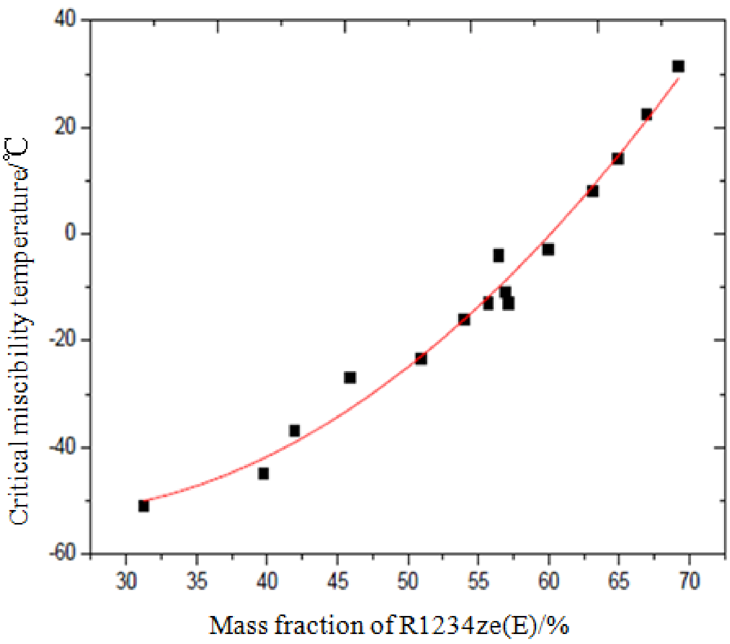


Figure 3 The critical miscibility temperature of R1234ze(E)/RE170 with mineral oil.

As seen from the figure 3, when the mass fraction of R1234ze (E) was less than 31%, the critical miscibility temperature of RE170 / R1234ze (E) and mineral oil mixed solution was lower than -50℃, which present a good miscibility in that content; When the mass fraction of R1234ze (E) was more than 60%, the critical miscibility temperature was above 0℃ and increased rapidly. It is recommended that the mass fraction of R1234ze (E) should not more than 60% in using RE170 + R1234ze (E) mixed refrigerant containing mineral oil system. If not, the refrigerant system may produce large amounts of sediment, even appear layered, and will affect the equipment operation efficiency and service life. When the mass fraction of R1234ze (E) is higher than 70%, the mixed solution will generated a lot of floc even at room temperature.

3. Conclusion

In this paper, the miscibility measurements of mixture (R1234ze(E)/RE170 + mineral oil) are presented in a temperature ranged from - 50℃ to 40℃. For the mixed solution, the content of R1234ze(E) was more than 60%, the critical miscibility temperature of R1234ze(E)/RE170 with mineral oil will rise rapidly; the RE170 promoted the miscibility of mixture. In order to avoid the break down of refrigerant system, it is recommended that the mass fraction of R1234ze (E) should not over 60% .

References

[1] Honeywell Fluorine Products, 2008, Honeywell HFO-1234ze Blowing Agent.

[2] Higashi, Y., 2010. Thermo physical prophaer ties of HFO-1234yf and HFO-1234ze(E), k05, Int. Symp. Next-generation Air Conditioning and Refrigeration Technology , Tokyo, Japan.

[3] J. S. Brown, G. D. Nicola, C. Zilio, L. Fedele, S. Bobbo, F. Polonara, Subcooled Liquid Density Measurements and PvT Measurements in the Vapor Phase for trans-1,3,3,3-Tetrafluoroprop-1-ene (R1234ze(E)), J. Chem. Eng. Data. 57.12 (2012) 3710-3720.

[4] X. Meng, G. Qiu, J. Wu, I.M. Abdulagatov, Viscosity measurements for 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) and trans-1,3,3,3-tetrafluoropropene(R1234ze(E)), J. Chem. Thermodyn. 63 (2013) 24-30.

[5] Y. Higashi, K. Tanaka, T. Ichikawa, Critical parameters and saturated densities in the critical region for trans-1,3,3,3-tetrafluoropropene(HFO-1234ze(E), J. Chem. Eng. Data. 55 (2010) 1594-1597

[6] K. Tanaka, Y. Higashi, PρT Property Measurements for

trans-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)) in the Gaseous Phase , J. Chem. Eng. Data. 5 (2010) 5164-5168.

[7] Z. Yang, X. Wu, T. Tian, Flammability of Trans-1, 3, 3, 3-tetrafluoroprop-1-ene and Its Binary Blends, Eng. 91 (2015) 386-392.

[8] Brown, J. Steven, Claudio Zilio, and Alberto Cavallini. "Thermodynamic properties of eight fluorinated olefins." International Journal of Refrigeration 33.2 (2010): 235-241.

[9] Hossain, M.A., Onaka, Y., Miyara, A., 2012. Experimental study on condensat ion heat transfer and pressure drop in horizontal smooth tube for R1234ze(E), R32 and R410A. Int. J.Refrigeration 35, 927- 938.

[10] Hossain, Md Anowar, et al. "Heat transfer during evaporation of R1234ze (E), R32, R410A and a mixture of R1234ze (E) and R32 inside a horizontal smooth tube." international journal of refrigeration 36.2 (2013): 465-477.

[11] Fukuda, Sho, et al. "Low GWP refrigerants R1234ze (E) and R1234ze (Z) for high temperature heat pumps." International journal of Refrigeration 40 (2014): 161-173.

[12] Koyama, S., Takata, N., Fu kuda, S., 2011. An experiment al study on heat pump cycle using zeotropic binary refrigerant of HFO-1234ze(E) and HFC-32, 10th IEA Heat Pump Conference, Japan.

[13] Feidt, Michel, Abdelhamid Kheiri, and Sandrine Pelloux-Prayer. "Performance optimization of low-temperature power generation by supercritical ORCs (organic Rankine cycles) using low GWP (global warming potential) working fluids." Energy 67 (2014): 513-526.

[14] Jribi, Skander, et al. "Study on activated carbon/HFO-1234ze (E) based adsorption cooling cycle." Applied Thermal Engineering 50.2 (2013): 1570-1575.