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The investigation on the vapour liquid phase equilibrium of (ammonia + 1,1,1,2-tetrafluoroethane) system over the temperatures ranging from (243.150 to 283.150) K

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ABSTRACT

To blend ammonia with some hydrofluorocarbons may give these mixed refrigerants lower flammability and global warming potential. In this paper, the isothermal vapour liquid equilibrium (VLE) of (ammonia + 1,1,1,2-tetrafluoroethane) system at temperatures ranging from (243.150 to 283.150) K are presented. Two models were employed to regress the experimental VLE results, namely the Peng–Robinson (PR) equation of state with the simple van der waals (VDW) mixing rule; the Peng–Robinson equation of state combined non-random two-liquid (NRTL) activity coefficient model with the modified Huron-Vidal one-order (MHV1) mixing rule. The maximum average absolute relative deviation of pressure (AARD*p*) and average absolute deviation of the vapour phase mole fraction (AAD*y*) for PR-VDW are 0.56% and 0.010, respectively, while the maximum AARD*p* and AAD*y* for PR-MHV1-NRTL are 0.27% and 0.014, respectively. Positive azeotropic behaviour was exhibited at each temperature investigated.

1. Introduction

Ammonia (R717) is a refrigerant with excellent thermodynamic properties and has remained in continuous use as a refrigerant for more than one hundred years [1,2]. Ammonia is the best refrigerant synthetically considering volumetric capacity and coefficient of performance (COP) according to McLinden's work [3]. Besides, R717 is an environmentally friendly substance with very low global warming potential (GWP) and zero ozone depletion potential (ODP). However, due to its flammability, toxicity, strong odour and immiscibility with mineral oil, the use of ammonia is significantly restricted, especially in the civil field.

Searching for mixed refrigerants based on ammonia is one way to expand its application. The {ammonia (60% mass) + dimethyl ether (40% mass)} binary system has exhibited great advantages on the discharge temperature of the compressor, the solubility in mineral oils and the volumetric capacity [4,5]. Vapour liquid equilibrium (VLE) results provide the foundation for other mixed thermophysical properties. VLE data have been reported for (ammonia + n-butane) [6–8], (ammonia + propane) [9], (ammonia + 1-butene) [7], (ammonia + propene) [9] and (ammonia + pentafluoroethane) [10,11] systems. Hydrofluorocarbons show better inter-miscibility with ammonia relative to alkanes and alkenes. This is easy to understand from the intermolecular forces. The interaction force is much weaker between molecules with strong polarity and the hydrogen bond (ammonia for example) and molecules with weak polar (n-butane for example) than the interaction force between ammonia-ammonia or butane-butane. While for two different molecules (A and B) with similar polarity, the interaction force between A-B is close to the geometric mean of A-A and B-B [12]. On the other hand, 1,1,1,2-tetrafluoroethane (R134a), is also a refrigerant with good thermodynamic performance, zero ODP and non-flammability, while it has high GWP of 1430 [13]. To blend ammonia with 1,1,1,2-tetrafluoroethane may give this mixture lower flammability and GWP. In this paper, the isothermal VLE values for the (R717 + R134a) binary mixture at five temperatures are presented. The azeotropic behaviour was found at each temperature.

2. Experimental

2.1. Materials

Ammonia and 1,1,1,2-tetrafluoroethane were provided by Beijing AP BAIF Gases Industry Co., Ltd. All chemicals were analyzed by the gas chromatograph with the acceptable purity

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specifications (>0.999), so no further purification was performed. The mole fraction purities, critical parameters and acentric factors for R717 and R134a were shown in Table 1.

2.2. Apparatus

The apparatus has been described in detail in previous work [7] and was used without modification except for the platinum resistance thermometer and the chromatographic column. The schematic diagram of the experimental system is shown in Fig. 1. The VLE measurement was based on the vapour – phase single recirculation method by a magnetic pump driving the vapour through the liquid in the equilibrium cell. The equilibrium cell is immersed in an alcohol liquid bath, whose temperature is controlled by matching the heat loads from a refrigerator and an electrical heater.

A 25 Ω standard platinum resistance thermometer was used to measure the temperatures in the cell. The thermometer was calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences based on the 1990 International Temperature Scale with an uncertainty of ±3 mK. A FLUKE 1594A super thermometer provides temperature readings. A long-term temperature stability of ±3 mK can be achieved by software LABVIEW within at least 30 min. The standard uncertainty of the temperature measurement was less than ±5 mK.

A digital pressure transducer (Mensor Series 6000) was used to measure the pressures of the vapour phase in the cell. The uncertainty of pressure transducer is 0.0006 MPa with a full scale of 3.0 MPa. The fluctuation of the pressure is less than ±0.0001 MPa with the magnetic pump working. The standard uncertainty of the pressure measurement was less than ±0.0008 MPa.

A Beifen SP3400 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a GDX-101 column was used to measure the composition of the mixtures. The temperatures of the column and the detector were 313.15 K and 373.15 K, respectively. The GC was calibrated by the mixtures with known compositions gravimetrically. Eight groups of standard gas were measured. A standard curve was drawn with the multi-point correction method. Three analyses at least were carried out for each sample to make sure the maximum deviation among them was less than 0.002. Taking into account the uncertainties from the calibration and the dispersion of analyses, the standard uncertainty of the composition measurement was estimated to be less than ±0.005.

2.3. Experimental procedure

Firstly, the pipeline and the equilibrium chamber were evacuated and then be purged by R134a three times. Secondly, an amount of R134a was injected into the cell. When a given temperature was reached and the fluctuations of the temperature and the pressure were less than ±3 mK, ±0.0001 MPa, respectively, for more than 30 min in the cell, the equilibrium state was thought to be established. The saturated pressure of R134a was recorded. Then an estimated amount of ammonia was injected into the equilibrium cell. When the same equilibrium

Table 1
The CAS numbers, mole fraction purities, critical parameters (T_c, p_c), acentric factors ω, ODP, GWP and safety group for R717 and R134a.

Components	CAS No.	Mole fraction purities (stated by the supplier)	T_c/K [a]	p_c/MPa[a]	ω[a]	ODP[a]	GWP[a]	Safety Group[a]
R717[b]	7664-41-7	0.99999	405.40	11.333	0.25601	0	0	B2
R134a[b]	811-97-2	0.999	374.21	4.0593	0.32684	0	1430	A1

[a] From Ref. [12].
[b] Supplied by Beijing AP BAIF Gases Industry Co., Ltd.

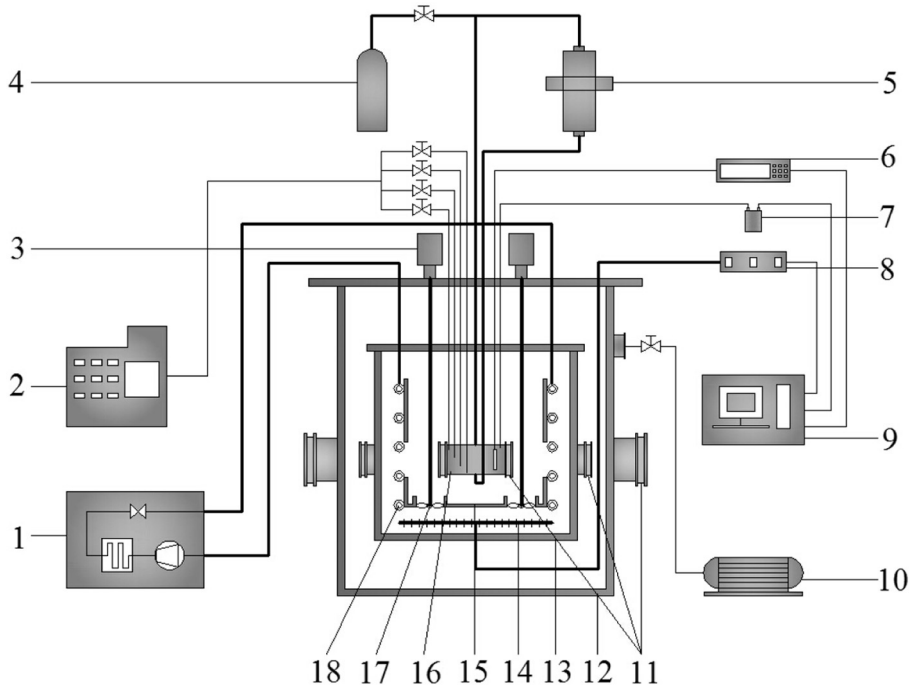

Fig. 1. Schematic diagram of the experimental system: 1. refrigerating machine; 2. gas chromatograph; 3. motor; 4. feed system; 5. magnetic pump; 6. thermometer; 7. pressure transducer; 8. stabilized voltage supply; 9. pressure and temperature indicator; 10. vacuum pump; 11. view windows; 12. vacuum vessel; 13. isothermal liquid bath; 14. electric heater; 15. diversion trench; 16. equilibrium cell; 17. stirrer; 18. cooling coil.