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Vapor Pressure of the 1,1,1,2-Tetrafluoroethane (R-134a) + Polyalkylene Glycol System

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Vapor pressures of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system were obtained at 72 points over the temperature range from 253.15 to 333.15 K at 10 K intervals and the composition range from 0 to 90 mass % polyalkylene glycol. It was found that below 273.15 K, the effect of the polyalkylene glycol on the vapor pressure was negligible up to 30 mass% polyalkylene glycol. The vapor pressure of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system decreased as the concentration of polyalkylene glycol increased. Raoult's model and Flory–Huggins model were used for data reduction. Raoult's model gave reasonable predictions for the vapor pressure of the system below 30 mass% polyalkylene glycol. The Flory–Huggins model gave reasonable predictions for the vapor pressure over the complete composition range. An empirical vapor pressure equation was obtained in terms of temperature and mass fraction polyalkylene glycol. The empirical equation was the most convenient way to calculate the vapor pressure.

KEY WORDS: mixture; polyalkylene glycol; R-134a; vapor pressure.

1. INTRODUCTION

1,1,1,2-tetrafluoroethane (HFC-134a) is recognized as an environmentally safe refrigerant in place of dichlorofluoromethane (CFC-12) which has been implicated in depletion of the ozone layer. In refrigerating machines, the refrigerant is mixed with lubricant oil. So, one of the key decisions to be made when introducing a new refrigerant is the choice of lubricant. The lubricant oil has significant effects on the thermophysical properties of the pure refrigerant such as vapor pressure, viscosity, and thermal conductivity. Particularly, the vapor pressure of the mixture system is critical

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in evaluating the performance of a refrigerating system and the miscibility and solubility of the mixture. Therefore, in this study the vapor pressure of the HFC-134a + lubricant oil system was investigated. Data for the vapor pressure for refrigerant + lubricant oil systems are scarce in the open literature.

Vapor pressures for the trifluoromethane (HCFC-22) + oil system were measured by Van Gaalen [1,2]. Vapor pressures for the trifluoromethane + naphthenic oil system were measured over the temperature range from 294.15 to 423.15 K and the composition range from 10 to 40 mass% lubricant oil [1]. Vapor pressures of the trifluoromethane + alkylbenzene system were measured over the temperature range 311.15 to 423.15 K [2]. Recently, Thomas and Pham [3] measured the vapor pressures of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system over the temperature range from 283.15 to 343.15 K and the composition range from 10 to 90 mass% polyalkylene glycol. In refrigeration, the evaporation temperature extends to less than 273.15 K. So, in this current study, the vapor pressures of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system were measured over the temperature range from 253.15 to 333.15 K at 10 K intervals and the composition range from 0 to 90 mass% polyalkylene glycol. In order to analyze the equilibrium behavior of the mixture system, Raoult's model and the Flory–Huggins model were tested as data reduction models. Also, based on the experimental data, an empirical working equation for the vapor pressure of the system was developed in terms of temperature and mass fraction polyalkylene glycol. Also, the effect of the polyalkylene glycol on the vapor pressure of the pure refrigerant was discussed.

2. EXPERIMENT

2.1. Chemicals

The samples of pure 1,1,1,2-tetrafluoroethane were obtained from Du Pont Co., and polyalkylene glycol was obtained from CPI Eng. The manufacturers stated that the purity of the chemicals was 99.9 mass%. The chemicals were used without further purification. Typical properties of the polyalkylene glycol and 1,1,1,2-tetrafluoroethane are listed in Table I.

2.2. Experimental Apparatus and Procedures

An experimental apparatus was developed to measure the vapor pressure of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system. The apparatus is shown schematically in Fig. 1. The apparatus, in general,

Table I. Properties of 46 ISO VG Polyalkylene Glycol and 1,1,1,2-Tetrafluoroethane

Items	Lubricant oil	Refrigerant
Company	CPI Eng.	Du Pont Co.
Chemicals	RPAG46	R-134a
Molar mass ($g \cdot mol^{-1}$)	1550	102.03
Viscosity ($Pa \cdot s$)	$46.52 \times 10^{-6} m^2 \cdot s^{-1}$(40°C)	287.4 (0°C)
Viscosity ($Pa \cdot s$)	9.47 $m^2 \cdot s^{-1}$ (100°C)	178.2 (40°C)
Density ($kg \cdot m^{-3}$)	975.4 (15.6°C)	1293.7 (0°C) 1146.5 (40°C)
Specific Gravity	0.978	1.23 (0°C)

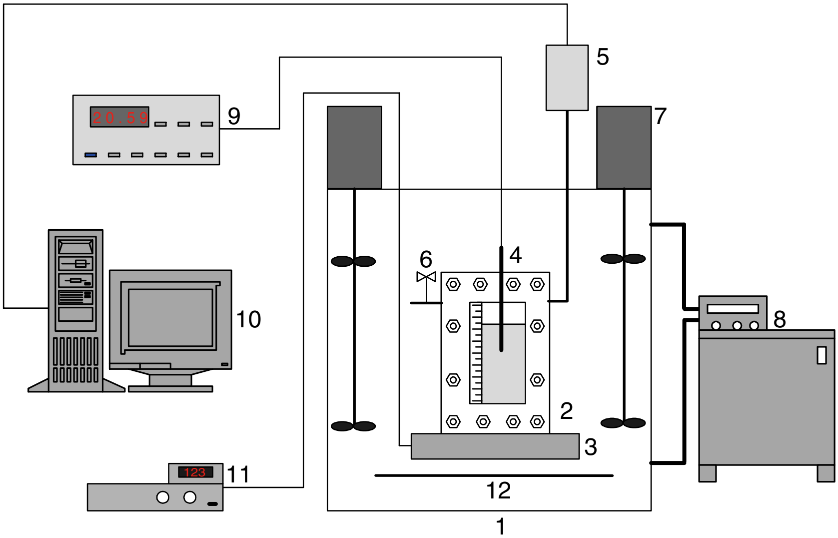

Fig. 1. Schematic diagram of the experimental apparatus. 1 – Constant temperature bath, 2 – Equilibrium cell, 3 – Magnetic stirrer, 4 – Resistance temperature detector, 5 – Digital pressure transducer, 6 – Charging valve, 7 – dc Motor and stirrer, 8 – Constant temperature bath (cold reservoir source), 9 – Digital thermometer, 10 – Personal computer, 11 – Magnetic stirrer controller, 12 – Heater.

consisted of an equilibrium unit, a temperature control unit, and a data measurement and acquisition unit. The equilibrium unit consisted of an equilibrium cell, a magnetic stirrer, and a thermostatic bath. The equilibrium cell was made of Type 316 stainless steel with an inner volume of about 72 cm^3 . In order to observe the inside of the cell, reinforced glass of 10 mm thickness was equipped in the front and rear plates of the cell.

Before starting a series of measurements, all parts of the equilibrium cell were cleaned. Then, they were assembled. The assembled equilibrium cell was evacuated to 10^{-3} torr. First, the mass of the evacuated cell was gravimetically determined. Second, the polyalkylene glycol was injected into the cell and the polyalkylene glycol-charged cell was again evacuated to 10^{-3} torr. Then, the mass of the polyalkylene glycol-charged cell was gravimetically determined. Third, 1,1,1,2-tetrafluoroethane was added into the polyalkylene glycol-charged cell and the mass of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol-charged cell was determined gravimetrically. Then, the mass percentage of the polyalkylene glycol was calculated. The precision of the balance (Sartorius F3200) was 0.1%. The uncertainty of the composition measurement was estimated to be 0.1%.

After calculating the mass percent polyalkylene glycol, the charged equilibrium cell was immersed in the thermostatic bath that was filled with silicon oil. The temperature of the isothermal bath and equilibrium cell was maintained at a set point by a cold reservoir, a heater, and circulator. It took 2 or 3 h for the temperature of the bath and cell to stabilize at a set point. After confirming that the bath and cell temperature were maintained at a set point within ±0.1 K, the magnetic stirrer in the equilibrium cell was started. It stirred the 1,1,1,2-tetrafluoroethane + polyalkylene glycol to ensure proper mixing, thus enabling equilibrium to be quickly reached. It took about 30 min for the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system to reach equilibrium to where the cell temperature was stable and the vapor–liquid boundary did not change. After equilibrium was reached, the bath and cell temperatures were measured with a 100 Ω platinum resistance sensor immersed in the cell and a precision thermometer (Yokogawa, 7563) with a precision of 0.01 K. The sensor and thermometer were calibrated on the ITS-90. The uncertainty in the temperature measurements was estimated to be ±0.1 K. The pressure was measured with a pressure transducer (Druck, PDCR 922) with a precision of 0.1 kPa. The pressure was recorded when the cell pressure was constant within 3 to 4 kPa. The pressure transducer was calibrated against a dead weight pressure gauge (Ruska, Budenberg) after each series of experiments. The uncertainty of the pressure measurement was estimated to be 0.2%. After a set of measurements was completed, the above procedure was repeated for another mass fraction of polyalkylene glycol.

3. RESULTS AND DISCUSSION

Before measuring the vapor pressure of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system, the vapor pressure of 1,1,1,2-tetrafluoroethane was measured in order to determine the accuracy of the experimental

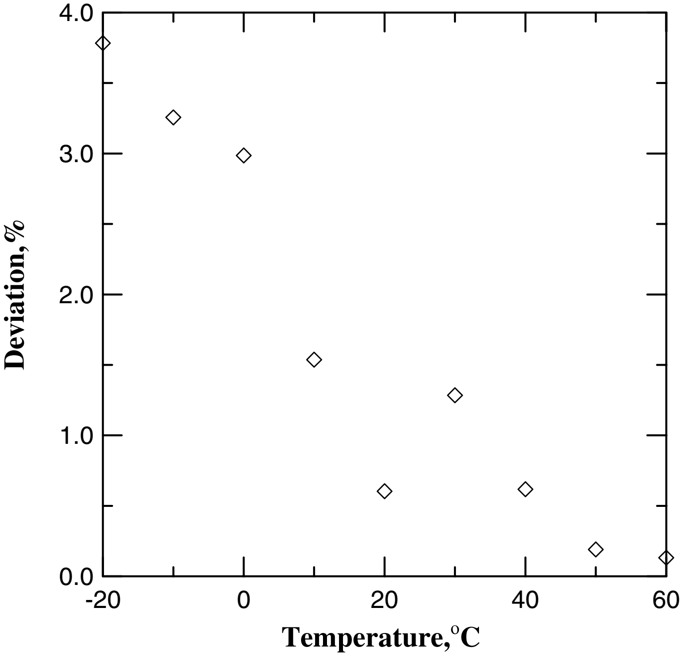

Fig. 2. Comparison of the measured vapor pressure of 1,1,1,2-tetrafluoroethane with data from ASHRAE [4].

apparatus. The measured vapor pressures of pure 1,1,1,2-tetrafluoroethane were compared with those of Ref. 4. The deviations are shown in Fig. 2. The root-mean-square deviation between the measured vapor pressures and those of Ref. 4 is 6.2 kPa or 2.1%. Thus, the accuracy of the experimental apparatus was demonstrated before the vapor pressure measurements on the refrigerant and oil system were commenced.

Based on the measured vapor pressures, a vapor pressure equation for the pure refrigerant was developed as follows:

$$\ln(P/P_c) = \frac{1}{1-\tau}\sum_{i=1}^{5} a_i \tau^{k_i} \quad 253.15 \leqslant T \leqslant 333.15 \tag{1}$$

where $\tau = T/T_c$, P is the vapor pressure (in kPa), T_c and P_c are the critical temperature (in K) and the critical pressure (in kPa), respectively, and the a_i coefficients from the least-squares fit are given in Table II.

The vapor pressures of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system were measured in a temperature range from 253.15 to

Table II. Coefficients of Vapor Pressure Eqs. (1)–(3)

	Eq. (1)	Eq. (2)	Eq. (3)
a_1	−10.2069	3.3277	4.4508
a_2	15.2548	872.5562	−0.0189
a_3	−18.6998	−296967.9754	3.86×10^5
a_4	9.9485	2.8309	−1.880
a_5	94.3221	−1710.4368	3.68×10^7
a_6		249712.5478	6.10×10^9
a_7		−0.1963	
a_8		116.1194	
a_9		−16891.8367	
k_1	1		
k_2	1.5		
k_3	2		
k_4	4		
k_5	6.5		

333.15 K at 10 K intervals over a composition range from about 4 to 92 mass% polyalkylene glycol. The measured vapor pressures are presented in Table III. Thomas and Pham [3] reported their measured data only plotted on figures. So, quantitative comparison with Ref. 3 was not possible in the present study.

The variation of the vapor pressure of the system with the concentration of polyalkylene glycol is presented in Fig. 3. The vapor pressure decreases as the concentration of polyalkylene glycol increases. The effect of polyalkylene

Table III. Measured Vapor Pressure Data for R-134a and PAG Oil Mixtures (Concentrations are given in mass% polyalkylene glycol.)

T (K)	Vapor Pressure (kPa)						
	0 mass%	10.12 mass%	20.37 mass%	30.38 mass%	50.91 mass%	71.07 mass%	91.55 mass%
253.15	137.1	128.5	125.0	120.6	116.4	100.1	42.60
263.15	207.0	192.5	186.9	180.8	172.8	152.7	57.35
273.15	301.4	280.1	246.1	238.9	227.9	200.2	79.65
283.15	420.8	393.9	381.9	342.2	318.2	261.5	108.1
293.15	575.0	542.0	525.6	486.3	473.8	358.1	141.6
303.15	779.9	753.8	744.3	733.3	669.0	525.4	175.1
313.15	1022	979.2	952.4	936.6	830.8	689.7	234.5
323.15	1320	1268	1232	1209	1105	876.8	357.6
333.15	1683	1633	1600	1579	1411	1133	465.6

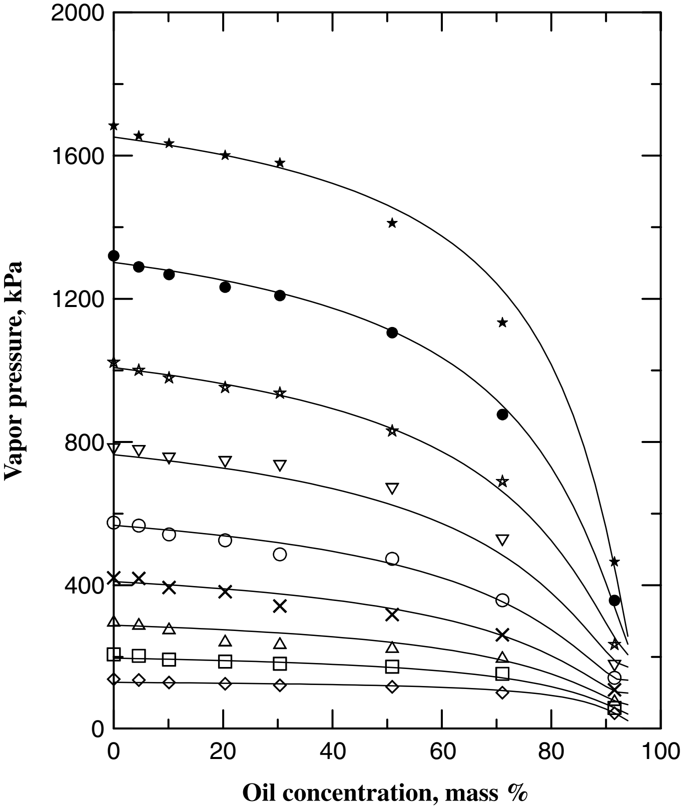

Fig. 3. Vapor pressure of 1,1,1,2-tetrafluoroethane + polyalkylene glycol as a function of temperature and polyalkylene glycol concentration: ◇ – 273.15 K; □ – 283.15 K; △ – 293.15 K; × – 303.15 K; ○ – 313.15 K; ▽ – 323.15 K; ☆ – 333.15 K; ● – 343.15 K; ★ – 353.15 K.

glycol is more significant above 273.15 K. Below 273.15 K, the effect of polyalkylene glycol is negligible up to 30 mass % polyalkylene glycol.

Based on the measured data, a vapor pressure-temperature-mass percent (P-T-w) equation was empirically obtained. The empirical equation is as follows:

$$\ln P(\omega, T) = (a_1 + a_2/T + a_3/T^2) + (a_4 + a_5/T + a_6/T^2)/\omega + (a_7 + a_8/T + a_9/T^2)/\omega^2 \qquad (2)$$

where P is the vapor pressure in kPa, T is the temperature in K, ω is the composition in mass %, and a_1 to a_9 are coefficients determined by least squares. The empirical Eq. (2) was compared with another type of empirical equation by Cavestri [5] that was a function of mass fraction polyalkylene glycol, temperature, and saturation pressure of the pure 1,1,1,2-tetrafluoroethane of the system at the same temperature.

$$P(\omega, T) = \omega P_{\text{sat}}(T) + \omega(1-\omega) \times (a_1 + a_2 T + a_3 T^2 + a_4\omega + a_5\omega T + a_6\omega T^2) P_{\text{sat}}(T) \qquad (3)$$

P is the vapor pressure in kPa, P_{sat} is the saturation pressure in kPa, T is the temperature in K, and ω is the mass fraction in percent. Coefficients of the vapor pressure Eqs. (1–3) are reported in Table II.

In order to investigate the accuracy of these equations, the root-mean-square deviations between measured and calculated vapor pressures from the two empirical equations are presented in Table IV. In Fig. 4, the measured vapor pressures were compared with the calculated pressures from Eq. (2). The average root-mean-square deviation of Eq. (2) is 4.2%, as shown in Table IV.

4. DATA ANALYSIS

4.1. Raoult's Model

As the partial pressure of polyalkylene glycol in the vapor phase is negligible compared to that of 1,1,1,2-tetrafluoroethane, the vapor pressure

Table IV. Root-Mean-Square Deviations between Measured Vapor Pressures and Those Calculated from Empirical Equations for 1,1,1,2-Tetrafluoroethane + Polyalkylene Glycol

Lubricant oil concentration (mass%)	RMS % deviation from measured vapor pressure	
	Eq. (2)	Eq. (3)
0	3.41	0.73
4.58	2.64	1.32
10.12	1.15	1.02
20.37	4.26	3.34
30.38	5.89	4.48
50.91	3.77	4.15
71.07	5.45	8.11
91.55	4.68	11.48
Average	4.16	5.62

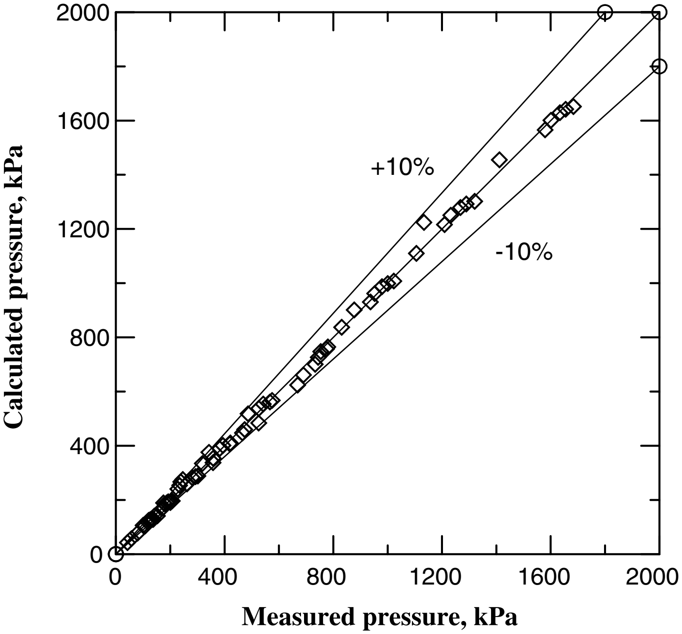

Fig. 4. Comparison of the measured vapor pressure of 1,1,1,2-tetrafluoroethane + polyalkylene glycol with the empirical equation.

of the 1,1,1,2-tetrafluorothane + polyalkylene glycol system is assumed to be equal to the vapor pressure of the 1,1,1,2-tetrafluoroethane, as follows [6]:

$$P_{r,\text{vap}} = P_{\text{vap}} = x_{\text{ref}} P_{\text{sat,ref}}(T) \tag{4}$$

$P_{r,\text{vap}}$ is the partial pressure of the refrigerant 1,1,1,2-tetrafluoroethane in the vapor phase, P_{vap} is the pressure of the refrigerant in the vapor phase, x_{ref} is the mole fraction of the 1,1,1,2-tetrafluoroethane in the liquid phase, and $P_{\text{sat,ref}}$ is the saturation vapor pressure of the pure 1,1,1,2-tetrafluoroethane.

In Fig. 5, measured vapor pressures of the system were compared with predicted pressures from Raoult's model. In Table V, root-mean-square deviations between the measured and predicted values are presented. Below 5 mass% polyalkylene glycol, Raoult's law gave predicted values in reasonable agreement with the measured data. However, as the concentration of polyalkylene glycol increased, Raoult's model predicted significantly larger values than the measured data.

Table V. Root-Mean-Square Deviations for Raoult's Model and Flory–Huggins Model

Lubricant oil concentration (mass%)	RMS % deviation from the measured data	
	Raoult's Law	Flory–Huggins theory
0	1.91	–
4.58	1.63	2.65
10.12	5.12	3.61
20.37	9.06	6.93
30.38	12.63	8.50
50.91	15.41	8.70
71.07	29.14	8.38
91.55	126.90	11.83
Total	46.72	7.80

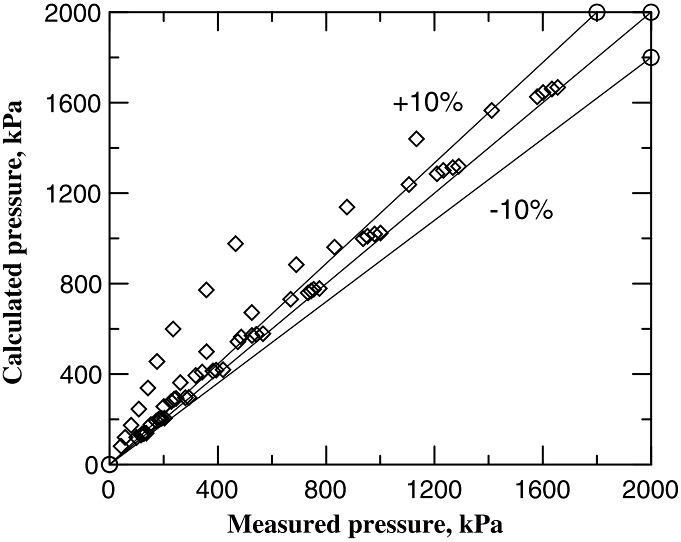

Fig. 5. Comparison of the measured vapor pressure of 1,1,1,2-tetrafluoroethane + polyalkylene glycol with Raoult's model.

4.2. Flory–Huggins Model

In the binary solution where the difference between the molar masses of two components is significant, the equilibrium behavior deviates significantly from Raoult's model. Thus, the equilibrium behavior of refrigerant and lubricant systems cannot be accurately predicted by Raoult's model. It is because the molar mass of the lubricant is an order of magnitude larger than that of the refrigerant. Thomas and Pham [3] suggested that the Flory–Huggins model could be used to predict the equilibrium properties of refrigerant and lubricant systems.

In the Flory–Huggins model [7], the ratio of the pressure of the system to that of the pure refrigerant is presented in terms of the Flory–Huggins interaction parameter x as follows:

$$\ln(P/P_{\mathrm{sat},1}) = \ln\phi_1 + \left(1 - \frac{1}{m}\right)\phi_2 + x\phi_2^2 \tag{5}$$

where

$$\phi_1 = \frac{f_1/\rho_1}{f_1/\rho_1 + f_2/\rho_2} \tag{6}$$

$$\phi_2 = \frac{f_2/\rho_2}{f_1/\rho_1 + f_2/\rho_2} \tag{7}$$

$$m = \frac{v_2^L}{v_1^L} \tag{8}$$

P is the vapor pressure of the refrigerant in kPa, P_{sat} is the saturation pressure of the refrigerant in kPa, f_i and ρ_i ($\mathrm{kg \cdot m^{-3}}$) are the mass fraction and density of component i, respectively, and v_i is the liquid specific volume ($\mathrm{m^3 \cdot kg^{-1}}$) of component i. The Flory–Huggins interaction parameter x is calculated by the least-squares method that minimizes the difference between the measured data and the predicted values. In this study the parameter x is 1.384 over the temperature range from 253.15 to 333.15 K.

In Fig. 6, the measured data are compared with the predicted values from the Flory–Huggins model. The predicted values from the model agreed reasonably well with the measured data over the complete composition range of polyalkylene glycol. In Table V, the results from the Flory–Huggins model are presented and compared with those from Raoult's model. The Flory–Huggins model was much better than Raoult's model for calculating the vapor pressures of the mixture considered in this study.

5. CONCLUSIONS

Vapor pressures of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system were obtained at 72 points over the temperature range from 253.15 to 333.15 K at 10 K intervals and the mass fraction ranged from 0 to 90% polyalkylene glycol.

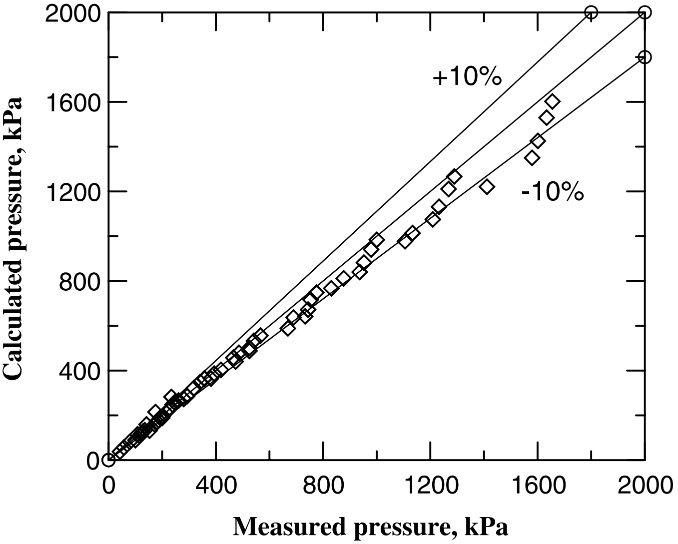

Fig. 6. Comparison of the measure vapor pressure of 1,1,1,2-tetrafluoroethane + polyalkylene glycol with the Flory–Huggins model.

1. It was found that the vapor pressure of the 1,1,1,2-tetrafluoroethane + polyalkylene glycol system decreased as the concentration of polyalkylene glycol increased. Below 273.15 K, the effect of the polyalkylene glycol on the vapor pressure was negligible up to 30 mass% polyalkylene glycol. The effect was significantly larger as the polyalkylene glycol increased over 50 mass%.

2. Raoult's model and Flory–Huggins model were tested for predictions of vapor pressures of the mixture. It was found that Raoult's model could be used for accurate predictions of the vapor pressure of the system below 30 mass% polyalkylene glycol. The Flory–Huggins model could be used for accurate predictions of the vapor pressure over the complete composition range of the mixture.

3. Also, an empirical vapor pressure equation was presented in terms of temperature and composition (mass%). The empirical equation is the most convenient method to predict the vapor pressure of the mixture. The average root-mean-square deviation between the experimental data and the calculated results from the equation was 4.2%.

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