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Saturated Pressure Measurements of 2,3,3,3-Tetrafluoroprop-1-ene (R1234yf) for Reduced Temperatures Ranging from 0.67 to 0.93

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ABSTRACT: 2,3,3,3-Tetrafluoroprop-1-ene (R1234yf) is one of the most promising alternative refrigerants because of its low global warming potential and a vapor pressure similar to 1,1,1,2-tetrafluoroethane (R134a). At present, its measured thermodynamic properties are scarce. Herein, vapor pressure data measurements and corresponding correlations are discussed. In particular, 40 vapor pressure measurements in the temperature range between (245.65 and 343.15) K were obtained, and these results, together with available literature data, were regressed using Wagner-type and extended Antoine-type equations. The normal boiling temperature for R1234yf was calculated to be 243.71 K.

INTRODUCTION

Nowadays, there is much interest in working fluids, e.g., refrigerants, possessing low global warming potential (GWP). There are many reasons for this, but one important factor is the growing number of regulations, taxes, laws, and agreements at the local, national, and international levels. Some recent examples include (1) the Kyoto Protocol, (2) some Scandinavian countries imposing Hydrofluorocarbon (HFC) taxes, (3) two proposed United States congressional legislative actions, and (4) the European Union's F-Gas regulations.

1. The Kyoto Protocol[1] is a framework which identifies six so-called basket-of-gases, among which HFC refrigerants play a part, and provides target global warming gas emissions by country.
2. Denmark, Norway, and Sweden tax HFC refrigerants.[2] These taxes are based on the mass of refrigerant and the refrigerant's GWP. For example, for 1 kg of R134a, these taxes translate to roughly 20 Euros for Denmark, 28 Euros for Sweden, and 34 Euros for Norway.
3. The 111th U.S. Congress proposed two legislative actions,[3,4] neither of which became law, to regulate HFCs under the United States Clean Air Act. Two of its major features would be to begin requiring the purchase of carbon offsets for the production and consumption of HFCs after 2012 and to reduce the HFC production and consumption by 85% from the baseline value (an average of amounts from 2004 to 2006) by 2032.
4. The European Union's F-Gas regulations[5,6] regarding the use of R134a in automotive applications have been introduced. In particular, these regulations specify that beginning on 1 January 2011 new models and on 1 January 2017 new vehicles fitted with air-conditioning cannot be manufactured with fluorinated greenhouse gases having GWP greater than 150.

Recently, fluorinated propene isomers have been proposed as possible refrigerants possessing low GWP values. Brown[7] lists nineteen possible fluorinated propene isomers possessing "bases"0 of 1225, 1234, and 1243, i.e., isomers containing 1 H/5 F, 2 H/4 F, and 3 H/3 F, respectively, although several of these likely have high levels of toxicity and are mildly to highly flammable. Note: isomers with "bases" of 1216, 1252, and 1261 were not considered because they are highly toxic and/or highly flammable. Of the isomers being investigated, two of them are actively being commercialized: R1234ze(E) (trans-1,3,3,3-tetrafluoroprop-1-ene; $CF_3CH{=}CHF$), which has a 100-year time horizon GWP of 6 relative to carbon dioxide,[8] and R1234yf (2,3,3,3-tetrafluoroprop-1-ene; $CF_3CF{=}CH_2$), which has a 100-year time horizon GWP of 4 relative to carbon dioxide[9] and is being actively pursued as a possible replacement fluid for R134a in automotive applications.[10]

While much R1234yf development work has been underway in the automotive industry over the past few years, thermodynamic and transport property data, and associated Equations of State (EoS), have only begun appearing in the open literature. In particular, experimental data are reported in the literature for critical state properties,[11,12] vapor pressure,[12−15] liquid density,[12,14,16] pressure−temperature-density in the vapor phase,[15,17] specific heat at constant pressure,[16] surface tension,[12] and liquid viscosity.[14] Several EoS are presented: extended corresponding states (ECS) EoS,[14,18] Martin−Hou (MH) EoS,[17,19] Patel−Teja (PT) EoS,[18] Peng−Robinson (PR) EoS,[20,21] and FEQ Helmholtz EoS.[22]

This paper presents new vapor pressure measurements for R1234yf and R134a at temperatures ranging from approximately (245.7 to 343.2) K, develops a Wagner-type and an extended Antoine-type vapor pressure correlation, and compares the existing publically available vapor pressure data to the existing vapor pressure correlations and to a newly developed one.

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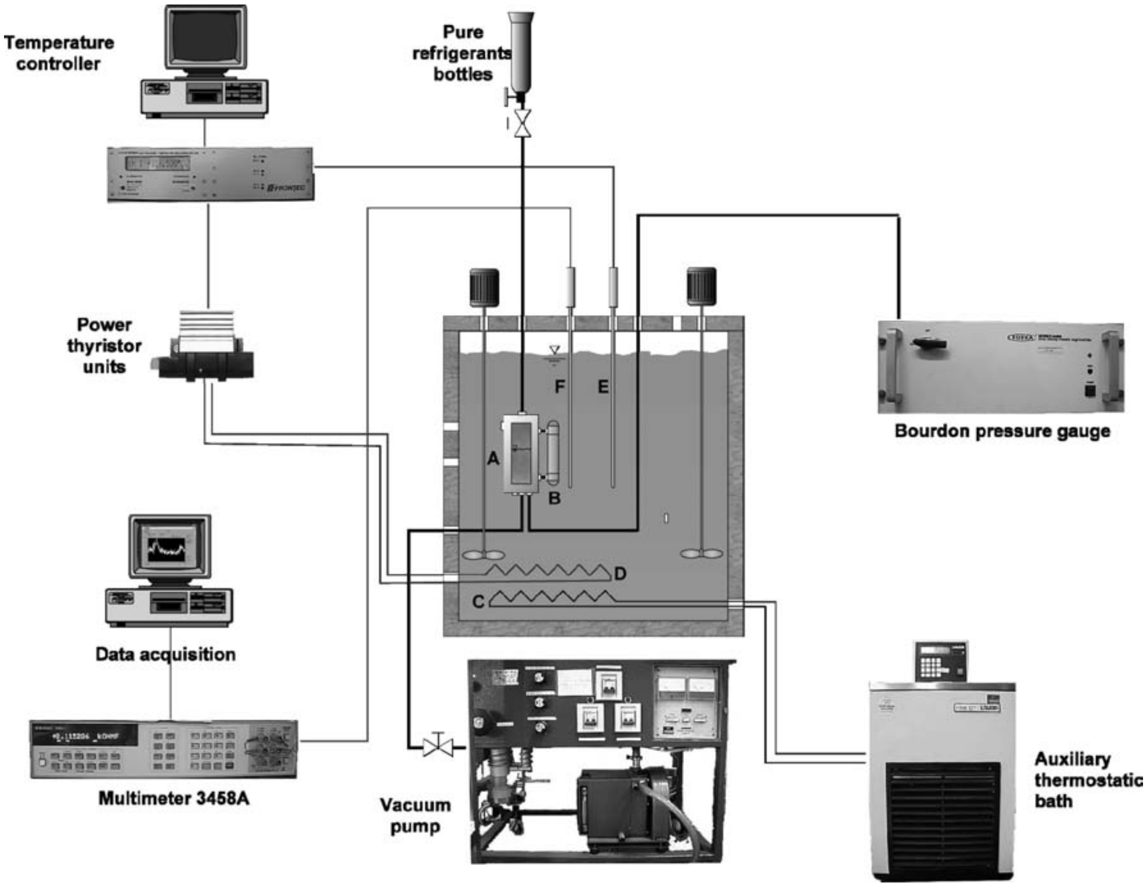

Figure 1. VLE apparatus. A = equilibrium cell, B = magnetic pump, C = cooler, D = thermal resistance, E = PID control reference thermometer, and F = measurements thermometer.

■ EXPERIMENTAL SECTION

Materials. R1234yf (2,3,3,3-tetrafluoroprop-1-ene, $CF_3CF{=}CH_2$, CAS number 754-12-1) was provided by DuPont with a declared purity higher than 99.5 wt %. R134a (1,1,1,2-tetrafluoroethane, CF_3CH_2F, CAS number 811-97-2) was supplied by Nevada with a purity higher than 99.5 wt %.

In order to eliminate noncondensable gases, each sample underwent several cycles of freezing with liquid nitrogen, evacuation, thawing, and ultrasound agitation. The samples were then used with no further purification.

Experimental Apparatus. Vapor pressure measurements were taken at isothermal conditions in the range between (245.65 and 343.15) K by means of a static vapor–liquid equilibrium apparatus, described in detail[23] and shown in Figure 1.

Equilibrium was reached in a stainless steel cell with a volume of about 50 cm^3. The cell contains a glass window and is equipped with a magnetic pump which is able to force the vapor phase into the liquid phase in order for the sample to reach a faster equilibrium. The cell was immersed in a 100 L thermostatic water and ethylene glycol bath to maintain the experimental temperature stability at ± 1 mK. Temperature was measured by means of a 100 Ω platinum resistance thermometer (ISOTECH 909/100), with an uncertainty of about 0.03 K, while pressure was measured with a pressure gauge (RUSKA 6000) with a full scale of 3.5 MPa, with an uncertainty around 1 kPa, including the accuracy of the pressure transducer and the stability of pressure during the measurements.

Experimental Procedure. The cell and the circuit were placed under vacuum for one day after which the sample was charged into the system. The meniscus between the liquid and vapor phases was established at the middle of the cell height. The thermostatic bath was stabilized at the desired temperature and the magnetic pump was activated for half an hour to facilitate attainment of equilibrium after which at least two hours passed before measurements were taken in order for the pressure to stabilize. The experimental vapor pressure was considered to be the average of at least five measurements taken approximately every 10 min, with a deviation lower than 0.1 kPa. After the vapor pressure was measured at one temperature, the temperature of the thermostatic bath was changed to the next desired value.

■ RESULTS AND DISCUSSION

Before presenting the vapor pressure measurements and accompanying correlations, the existing critical state properties, which are important for developing vapor pressure correlations and equations of state, will be briefly discussed.

Critical State Properties. Different critical properties can be found in the literature for R1234yf, i.e., a critical temperature (T_c) = 368.15 K and a critical pressure (P_c) = 3239 kPa,[11] or T_c = 367.85 K, P_c = 3382 kPa, and the critical density (ρ_c) = 478 kg m^{-3}.[12] The critical state properties reported by Spatz and Minor[11] do not include estimation for the accuracies; whereas, Tanaka and Higashi[12] estimate the accuracies to be ± 0.01 K, ± 3 kg m^{-3}, and ± 3 kPa for T_c, P_c, and ρ_c, respectively. Therefore, the critical

Table 1. Experimental Vapor Pressures for R134a Compared with the Refprop 9.0[22]

T	P_{exp}	P_{ref}	$P_{\text{ref}} - P_{\text{exp}}$	
K	MPa	MPa	MPa	$e_r = 100 \cdot (P_{\text{ref}} - P_{\text{exp}})/P_{\text{exp}}$
283.13	0.414	0.414	0.000	0.00
293.14	0.571	0.572	−0.001	−0.17
303.12	0.769	0.770	−0.001	−0.13
313.11	1.015	1.016	−0.001	−0.10
323.17	1.319	1.319	0.000	0.00
333.16	1.681	1.682	−0.001	−0.06
343.16	2.117	2.117	0.000	0.00

Table 2. Vapor Pressure Measurements for R1234yf by the Authors for T Ranging from Approximately (245.7 to 343.2) K

T	P_{exp}	T	P_{exp}
K	MPa	K	MPa
245.65	0.113	295.65	0.636
248.15	0.123	298.16	0.683
250.65	0.136	300.66	0.732
253.15	0.151	303.16	0.784
255.65	0.166	305.66	0.838
258.15	0.184	308.16	0.895
260.65	0.202	310.66	0.956
263.15	0.222	313.16	1.019
265.65	0.243	315.66	1.084
268.15	0.265	318.16	1.153
270.65	0.290	320.66	1.226
273.15	0.316	323.16	1.302
275.65	0.343	325.65	1.381
278.15	0.373	328.15	1.464
280.65	0.404	330.66	1.551
283.15	0.437	333.16	1.641
285.65	0.473	335.66	1.736
288.15	0.510	338.16	1.834
290.65	0.550	340.66	1.937
293.16	0.592	343.15	2.044

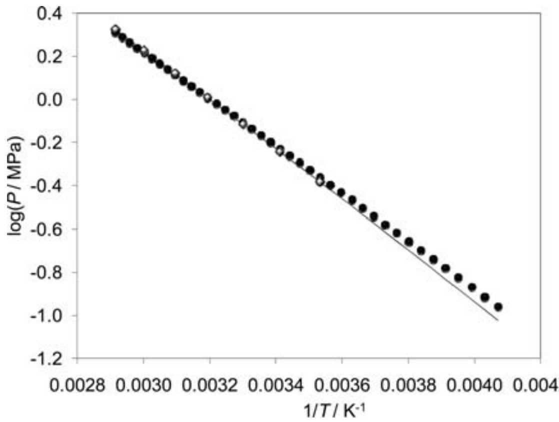

Figure 2. Experimental saturated pressure for (●) R1234yf and (◇) R134a. (—) Calculated saturated pressure by means of Refprop 9.0[22] for R134a.

Table 3. Constants for eqs 1 and 2 Derived from Literature,[12,13,15] **and the Data of Table 2**

	A_1	A_2	A_3	A_4	A_5	A_6
eq 1	−7.34421	1.49565	−1.77264	−4.92486		
eq 2	36.0219	−38.7224	−4.8149	−60.0244	13.8526	36.8462

state properties of Tanaka and Higashi[12] are used in the remainder of this paper.

Experimental Saturated Pressure. In order to check the reliability of the experimental setup, 7 vapor pressure data for R134a were measured between (283.13 and 343.16) K. The results are shown in Table 1, together with the deviations from Refprop 9.0,[22] which are well within the experimental uncertainties, confirming data consistency.

Hence, 40 R1234yf saturated pressure experimental data were measured between (245.65 and 343.15) K,[24] as shown in Table 2 and in Figure 2, where also comparisons with R134a vapor pressures is made. The saturated pressures for the two fluids are very similar.

Literature Saturated Pressure. Spatz and Minor[11] provide the vapor pressures (P_{vap}) for two temperatures (T): $P_{\text{vap}} = 0.673$ MPa at $T = 298.15$ K and $P_{\text{vap}} = 2.47$ MPa at $T = 353.15$ K, though it is unclear if these are measured or predicted values. In addition to these values, there have been a total of 85 experimental saturation pressure values published to-date in the open literature by different research groups that will be considered in the development of the correlations in this paper: 11 data points for T ranging from approximately (310 to 360) K,[12] 34 data points for T ranging from approximately (224 to 363) K,[13] 12 data points for T ranging from approximately (241 to 353) K,[14] and 28 data points for T ranging from approximately (250 to 320) K.[15] Herein, 40 data points (listed in Table 2) for T ranging from approximately (241 to 343) K are provided. Thus, there are approximately 125 experimental data points available for developing a vapor pressure correlation.

Vapor Pressure Correlations. Tanaka and Higashi[12] and Di Nicola et al.[13] provide Wagner-type vapor pressure correlations based on their experimental data, and Hulse et al.[14] and Leck[19] provide extended Antoine vapor pressure correlations based on their experimental data. [Note: There is a typographical error in the vapor correlation given by Di Nicola et al.[13] which was confirmed by Di Nicola.[25] The correct form of their correlation should be as follows: $\ln(T_r P_r) = A_1\tau + A_2\tau^{1.5} + A_3\tau^3 + A_4\tau^6$.]

As will be clarified below, the data of Hulse et al.[14] are not consistent with the other data sets. Therefore, only the 113 data points of Tanaka and Higashi,[12] Di Nicola et al.,[13] and Richter et al.[15] and the data of Table 2 were used to develop a Wagner-type vapor pressure correlation given in eq 1 and an extended Antoine-type vapor correlation given in eq 2.

$$T_r \ln(P_r) = A_1\tau + A_2\tau^{1.5} + A_3\tau^{2.5} + A_4\tau^5 \qquad (1)$$

$$\ln(P_r) = A_1 + \frac{A_2}{A_3 + T_r} + A_4 T_r + A_5 T_r^2 + A_6 \ln(T_r) \qquad (2)$$

with the constants given in Table 3 and where the reduced temperature $T_r = T/T_c$, the reduced pressure $P_r = P/P_c$, and $\tau = 1 - T_r$. Table 4 shows relative ($e_r = \Sigma_{i=1}^n e_i/n$) and absolute ($e_a = \Sigma_{i=1}^n e_i/n$) mean percentage errors for data from the four

Table 4. Relative and Absolute Mean Percentage Errors of Five Vapor Pressure Correlations

data set		eq 1	eq 2	eq 12	eq 13	eq 14	eq 21	eq 22
all 113 data points	e_r (%)	0.003	0.007	−0.136	0.012	−1.314	−0.233	0.03
	e_a (%)	0.075	0.121	0.371	0.108	1.314	0.292	0.091
literature data[12]	e_r (%)	−0.098	−0.127	0.011	−0.105	−2.221	−0.186	−0.122
	e_a (%)	0.111	0.165	0.035	0.114	2.221	0.186	0.122
literature data[13]	e_r (%)	−0.006	−0.009	−0.031	0.054	−1.306	−0.193	0.087
	e_a (%)	0.093	0.147	0.506	0.147	1.306	0.354	0.144
literature data[14]	e_r (%)	1.36	1.347	1.143	1.35	0.104	1.086	1.383
	e_a (%)	1.36	1.347	1.143	1.35	0.236	1.086	1.383
literature data[15]	e_r (%)	−0.022	−0.002	−0.194	−0.035	−1.488	−0.282	−0.028
	e_a (%)	0.066	0.124	0.317	0.106	1.488	0.282	0.05
Table 2	e_r (%)	0.055	0.065	−0.225	0.041	−0.949	−0.245	0.065
	e_a (%)	0.056	0.084	0.386	0.073	0.949	0.274	0.067

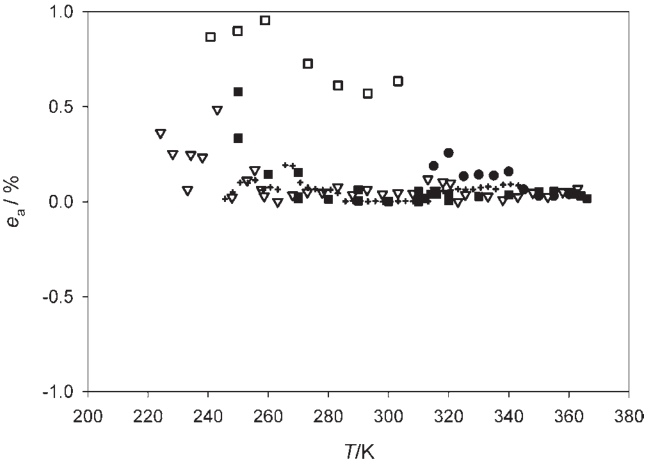

Figure 3. Relative mean percentage errors of data sets versus eq 1. (●) Tanaka and Higashi,[12] (∇) Di Nicola et al.,[13] (□) Hulse et al.,[14] (■) Richter et al.,[15] and (+) Table 2.

publicly available data sets, where the relative error $e_i = (y_{p,i} - y_{k,i})/y_{k,i} \times 100$, y is the property value, and the subscripts p,i and k,i refer to predicted and known, respectively, for the ith datum. In Figure 3, deviations from the available vapor pressure data sets from eq 1 are shown. It is evident all the data are consistent with each other, except those from Hulse et al.,[14] which show a systematic deviation with $e_a > 1$ %. For this reason, they were not included in the regression. Note: deviations among the measurements increase for temperatures lower than approximately 250 K.

While the correlations found in the literature,[12,13,21,22] and eqs 1 and 2 correlate the entire publicly available data set with $e_a < 0.4$, eq 1 provides the lowest value at $e_a < 0.075$.

Normal Boiling Point Temperature. Spatz and Minor[11] give the normal boiling point temperature (NBP) as 244.15 K, Tanaka and Higashi[12] report the NBP as 243.80 K (their source is a 2008 private communication), and eq 1 yields a NBP of 243.71 K.

CONCLUSIONS

Herein, 40 new vapor pressure measurements of R1234yf (2,3,3,3-tetrafluoroprop-1-ene; $CF_3CF{=}CH_2$) for reduced temperatures from (0.67 to 0.93) are presented, which represent approximately a third of the publically available measurements to-date from five research groups. All of the publicly available data sets, including the new measurements presented in Table 2, were used to develop two vapor pressure correlations: Wagner-type and extended Antoine-type. The Wagner-type vapor pressure correlation described in eq 1 provides the lowest $e_a = 0.075$ of the considered correlations. Finally, the normal boiling temperature of R1234yf is estimated to be 243.71 K.

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