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Accurate vapor pressure equation for refrigerants

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Abstract

This paper contains parameters for a universal vapor pressure equation describing methane, ethane, propane, n-butane, i-butane, R-11, R-12, R-22, R-23, R-32, R-123, R-124, R-125, R-134a, R-141b, R-142b, R-143a and R-152a. These parameters have been generated using experimental vapor pressures reported in literature. The vapor pressure equation, based upon asymptotic behavior at the triple and critical points, has three adjustable fluid-dependent parameters. This equation describes the entire vapor pressure curve within the apparent accuracy of the experimental values.

1. Introduction

Accurate vapor pressures are important for the design of process equipment, especially in the field of refrigeration and air conditioning. Many vapor pressure equations have appeared in the literature, but those which describe experimental data over the entire vapor pressure curve (from the triple point to the critical point) within the accuracy of the measurements are complex. Alternatively, simple functions such as the Antoine equation can describe vapor pressures accurately over a limited range of temperatures. Recently, Iglesias-Silva et al. (1987) have reported an equation which describes vapor pressures accurately over the entire vapor pressure curve using only three fluid-dependent parameters in addition to the temperatures and pressures at the triple and critical points. Iglesias-Silva et al. (1987) present a comparison of this equation with existing vapor pressure equations.

This work reports the application of the Iglesias-Silva et al. (1987) equation to a variety of fluids which are important to the refrigeration and air conditioning industry for which experimental

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measurements are available in the literature. The fluid dependent parameters have been determined for several hydrocarbon and halocarbon substances, and minor adjustments have been made to the triple and critical point pressures (within the accuracy of the reported measurements) to provide the best descriptions of experimental measurements for each fluid.

2. Vapor pressure equation

The Iglesias-Silva et al. (1987) vapor pressure equation results from a method proposed by Churchill and Usagi (1972), Churchill and Usagi (1974) for correlation development which is especially useful given known asymptotic behavior of the function. For vapor pressure, the asymptotic behaviors near the triple and critical points each are available, and, according to the Churchill–Usagi approach, they combine as

$$p(t) = \left\{ [\, p_0(t)]^N + [\, p_\infty(t)]^N \right\}^{1/N} \tag{1}$$

where the subscripts 0 and ∞ denote the asymptotic limits approaching the triple and critical points respectively. The reduced pressures and temperatures are

$$p = 1 + \frac{P^\sigma - P_t}{P_c - P_t} \tag{2}$$

$$t = \frac{T - T_t}{T_c - T_t} \tag{3}$$

thus $0 < t < 1$ and $1 < p < 2$. The asymptote approaching the triple point comes from application of the Clausius–Clapeyron equation along with the assumption that the enthalpy of vaporization varies linearly with temperature. Iglesias-Silva et al. (1987) provide details of the derivation. The expressions provided by Iglesias-Silva et al. (1987) are (after rearrangement):

$$P_0(t) = 1 - \frac{P_t}{P_c - P_t}\left\{1 - [1 + At]^s \exp\left(\frac{Art}{1 + At}\right)\right\} \tag{4}$$

where

$$A = \frac{T_c - T_t}{T_t} = \frac{T_c}{T_t} - 1 \quad r = \frac{b_1}{RT_1} - \frac{b_0}{R} \quad s = \frac{b_0}{R}$$

where b_0 and b_1 are fluid dependent parameters which result from least square fits.

The asymptote approaching the critical point results from assuming the scaling hypothesis along with simple background terms. Iglesias-Silva et al. (1987) again provide details:

$$p_\infty(t) = 2 - a_4(1 - t) + a_5(1 - t)^{2-\Theta} + a_6(1 - t)^3 + a_7(1 - t)^4 \tag{5}$$

Iglesias-Silva et al. (1987) also present simple relations for the parameters a_5, a_6 and a_7 in Eq. (5) in terms of a_4:

$$a_5 = -0.11599104 + 0.29506258a_4^2 - 0.00021222a_4^5$$

$$a_6 = -0.01546028 + 0.08978160a_4^2 - 0.05322199a_4^3$$

$$a_7 = 0.05725757 - 0.06817687a_4 + 0.00047188a_4^5$$

Therefore, only a_4 in Eq. (5) remains as a fluid-dependent fit parameter.

Walton et al. (1978) suggest that $\Theta = 0.199$ provides the optimal representation of experimental data. Therefore, although the scaling hypothesis suggests that the value should be lower, we use $\Theta = 0.2$ for this work. Finally, Iglesias-Silva et al. (1987) have shown that the empirical exponent N may be calculated from the reduced triple point temperature

$$N = 87T_t/T_c \tag{6}$$

Finally, only a_4, b_0, and b_1 remain as fluid-dependent parameters.

3. Fitting procedure

Standard nonlinear statistical procedures of the form available in commercial statistical packages provide estimates of the equation parameters. The optimal representation occurs when the measure-

Table 1
Critical and triple point temperatures and pressures used for fits

Substances	Formula	T_c/K	P_c/KPa	T_t/K	P_tkPa
Methane	CH_4	190.551	4599.2	90.685	11.696
Ethane	CH_3CH_3	305.33	4871.4	90.348	0.0011308
Propane	$CH_3CH_2CH_3$	369.85	4247.46	85.470	1.670×10^{-7}
i-Butane	$C(CH_3)_3$	407.85	3640.	113.55	1.9481×10^{-5}
n-Butane	$CH_3(CH)_2CH_3$	425.16	3796.	134.86	6.7352×10^{-4}
R-11	$CFCl_3$	471.15	4489.1	162.15	0.00663
R-12	CF_2Cl_2	384.95	4124.	115.19	0.00022
R-22	CHF_2Cl_2	369.30	4988.	113.	0.00021
R-23	CHF_3	299.30	4858.	113.2	0.025
R-32	CH_2F_2	351.56	5828.	137.	0.056
R-123	$CHCl_2CF_3$	456.831	3661.8	166.	0.005
R-124	$CHClCF_4$	395.425	3621.6	74.	3.0×10^{-13}
R-125	CHF_2CF_3	339.41	3638.86	169.817	2.5
R-134a	CH_2FCF_3	374.18	4056.	169.861	0.42
R-141b	$CFCl_2CH_3$	477.5	4194.	163.	0.0024
R-142b	CF_2ClCH_3	410.29	4041.	142	0.014
R-143a	CF_3CH_3	346.2	3811.	161.82	1.18
R-152a	CHF_2CH_3	386.44	4520.	154.6	0.065

ments are weighted statistically to reflect inaccuracies of the experimental measurements. The parameters chosen minimize the sum of the weighted squares of the differences between the calculated and observed values:

$$SS = \sum_{i=1}^{m} W_i[\Delta p_i]^2 \tag{7}$$

Two weighting methods were considered for this work: one suggested by Hust and McCarty (1967) and another suggested by Hall and Waxman (1974). We have compared the results using these methods for several substances. Having observed no significant differences, we have chosen to use the Hall–Waxman method:

$$W_i = \left\{\sigma_i(P) + \left|\frac{dP}{dT}\right|\sigma_i(T)\right\}^{-2} \tag{8}$$

We use the estimated inaccuracies in the measurements (as reported by the experimenters) for the standard deviations, σ, in Eq. 8. Application of Eq. (8) requires calculation of the derivative of the vapor pressure with respect to temperature. Because only modest accuracy is required, reasonable values result from first fitting an Antoine equation to the experimental data, then using the resulting Antoine constants to calculate temperature derivatives to fit the Iglesias-Silva et al. (1987) equation.

4. Results

The critical and triple point values used for these fits appear in Table 1. These values are available from the literature, but some pressures have been adjusted slightly (within the experimental uncer-

Table 2
Fit parameters and goodness of fit

Substances	a_4	b_0	b_1	AAPE
Methane	3.159535	−19.77081	8812.417	0.03
Ethane	4.581460	−36.42229	17877.435	0.07
Propane	5.205689	−43.50273	24771.221	0.07
i-Butane	4.999256	−47.83018	28197.481	0.54
n-Butane	4.797703	−43.85128	28605.450	0.51
R-11	4.622187	−42.90898	30785.831	0.24
R-12	4.826639	−46.09242	25758.054	0.12
R-22	4.911050	−49.29769	26059.761	0.09
R-23	4.563538	−44.54006	20546.185	0.26
R-32	4.540176	−40.63015	23777.844	0.44
R-123	4.703179	−49.81709	33076.999	0.40
R-124	6.135696	−46.82707	31078.738	0.33
R-125	3.738867	−36.65753	22158.209	0.15
R-134a	4.164859	−45.37032	26233.885	0.33
R-141b	4.615764	−56.66991	33952.289	0.08
R-142b	4.654313	−52.25382	28846.893	0.36
R-143a	3.966596	−31.40616	21960.232	0.30
R-152a	4.425958	−46.33295	26628.126	0.25

Table 3
Experimental data references

Substances	Reference	Authors
Methane	1	Kleinrahm and Wagner (1986)
Ethane	2	Goodwin et al. (1976)
Propane	3	Goodwin and Hayes (1976)
i-Butane	4	Goodwin and Hayes (1982)
n-Butane	5	Haynes and Goodwin (1982)
R-11	6	Fernandez-Farsnach and Del Rio (1985)
	7	Wang et al. (1991)
	8	Yurttas et al. (1990)
	9	Osborne et al. (1941)
R-12	10	Michels et al. (1966)
	11	Fernandez-Farsnach and Del Rio (1985)
	12	Händel et al. (1992)
R-22	13	Benning and McHarness (1940)
	14	Kohlen et al. (1985)
	15	Hongo et al. (1990)
	16	Händel et al. (1992)
	17	Niesen et al. (1994)
	18	Goodwin et al. (1992a)
R-23	19	Hou and Martin (1959)
	20	Valentine et al. (1962)
	21	Piacentini and Stein (1962)
	22	Stein and Proust (1977)
	23	Hori et al. (1982)
R32	24	Malbrunot et al. (1968)
	25	Widiatmo et al. (1994)
	26	Zhu et al. (1993)
	27	Holcomb et al. (1993)
	28	Weber and Goodwin (1993)
	29	Kanungo et al. (1987)[a]
R125	30	Holste (1994)
	31	Oguchi et al. (1994)
	32	Defibaugh and Morrison (1992)
R123	33	Weber (1990)
	34	Kubota et al. (1989)
	35	Piao et al. (1991)
	36	Oguchi et al. (1992)
	37	Goodwin et al. (1992b)
	38	Morrison and Ward (1991)
	39	Weber (1992)
R124	40	Niesen et al. (1994)
	41	Shankland et al. (1990)
	42	Boyes and Weber (1994)

Table 3 (continued)

Substances	Reference	Authors
R134a	43	Weber (1989)
	44	Kubota et al. (1989)
	45	Maezawa et al. (1990)
	46	Basu and Wilson (1989)
	47	Magee and Howley (1992)
	48	Blanke et al. (1994)
	49	Niesen et al. (1994)
	50	Goodwin et al. (1992b)
	51	Zhu et al. (1992)
	52	Morrison and Ward (1991)
	53	Baehr and Tillner-Roth (1991)
R141b	54	Weber (1992) [a]
	55	Weber (1992) [a]
	56	Defibaugh et al. (1993) [a]
	57	Holste (1994)
R142b	58	Mears et al. (1955)
	59	Yada et al. (1991)
	60	Silva and Weber (1993)
R143a	61	Mears et al. (1955)
	62	Russel et al. (1944)
	63	Widiatmo et al. (1994)
R152a	64	Baehr and Tillner-Roth (1991)
	65	Blanke et al. (1994)
	66	Iso and Uematsu (1989)
	67	Zhao et al. (1991)
	68	Higashi et al. (1987)
	69	Silva and Weber (1993)
	70	Holcomb et al. (1993)

[a] Zero weight in the fit.

tainty reported in the literature) to provide better agreement in the fits. In cases for which the triple point values are not available, the freezing point provides a good reference point because usually little difference exists between the freezing and triple point temperatures. The parameters a_4, b_0 and b_1 are provided for the light hydrocarbons (these are better values than those presented by Iglesias-Silva et al., 1987 because of an improved weighting procedure) and for those halocarbons for which sufficient experimental measurements are available from the literature to obtain a legitimate fit of the parameters. The resulting values are in Table 2 along with the averages of the absolute values of the deviations between the experimental values and those calculated from the equation. Table 3 identifies the data sources for each fluid.

Fig. 1 illustrates typical deviations between the experimental and calculated values for R-11, R-12, R-22, R-32 (methane based refrigerants) while Fig. 2 illustrates similar deviations for R-125, R-134a, R-141b and R-152a (ethane based refrigerants). All figures show that the equation is capable of describing the entire vapor pressure range within the estimated experimental uncertainties. Fig. 2 contains some hybrid log/linear plots. Such plots allow easy representation of data having widely different precisions/accuracies on a continuous axis. The systematic deviations in the plots are a

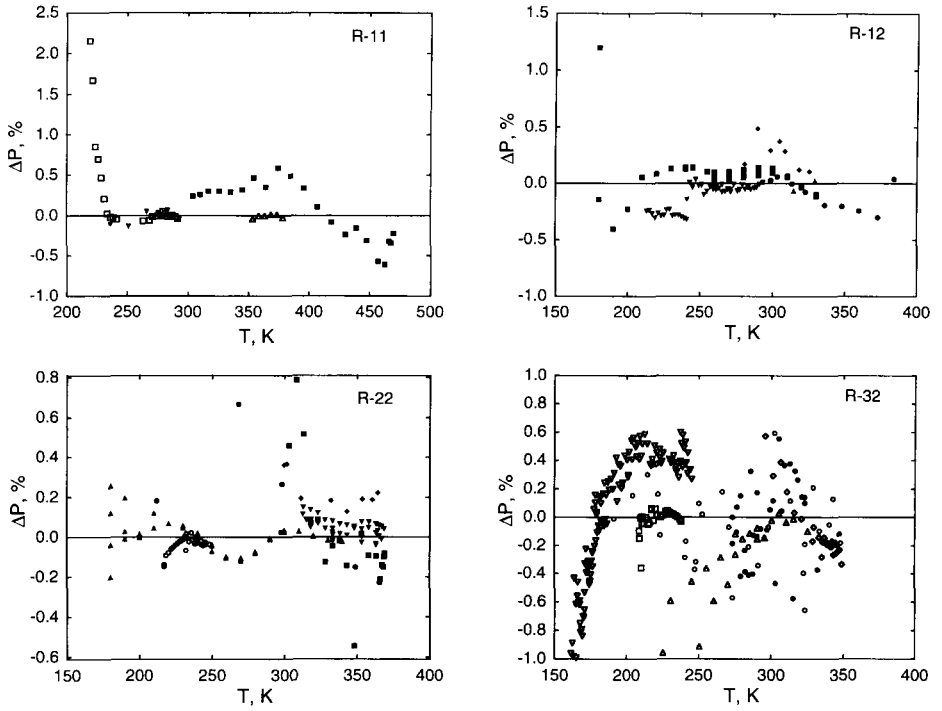

Fig. 1. Typical deviation plots for methane based refrigerants. Reference numbers from Table 3 with corresponding symbols: R-11 (□ 6, ■ 7, △ 8, ▽ 9), R-12 (● 10, ▼ 11, ■ 12), R-22 (● 13, ▼ 14, ■ 15, ▲ 16, ◆ 17, ○ 18), R-32 (○ 24, △ 25, ● 26, ◇ 27, □ 28, ▽ 29).

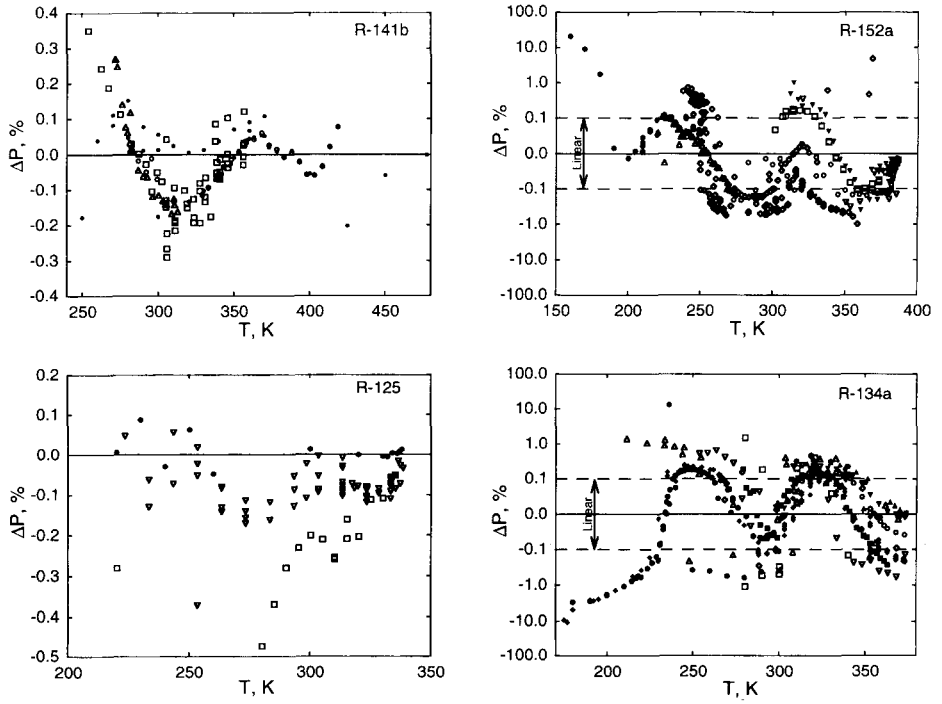

Fig. 2. Typical deviation plots for ethane based refrigerants. Reference numbers from Table 3 with corresponding symbols: R-125 (● 30, ▽ 31, □ 32), R-134a (○ 43, ▽ 44, □ 45, △ 46, ● 47, ◆ 48, ▲ 49, ⊙ 50, ■51, ◇ 52, ▼ 53), R-141b (○ 54, △ 55, □ 56, ● 57), R-152a (□ 64, ● 65, ▽ 66, ◇ 67, ○ 68, △ 69, ▼ 70).

result of using multiple data sets for the fits. The fit selects the optimal, weighted representation among the selected data.

5. List of symbols

AAPE	average absolute percentage error
a_i	parameters for vapor pressure equation
b_i	parameters for vapor pressure equation
N	empirical constant of vapor pressure equation
p	reduced vapor pressure variable
p^0	asymptotic vapor pressure behavior approaching triple point
p^∞	asymptotic vapor pressure behavior approaching critical point
Δp	difference between experimental and calculated values of p
P^σ	vapor pressure
P_c	critical pressure
P_t	triple point pressure
$\sigma(P)$	variance of temperature measurement
$\sigma(T)$	variance of temperature measurement
R	universal gas constant
SS	weighted sum of squares in statistical procedure
t	reduced temperature variable
T	temperature
T_c	critical temperature
T_t	triple point temperature
W_i	statistical weighting factor for datum i

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