New Equation of Saturation Pressure of Difluoromethane (HFC32)[1]

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ABSTRACT

Critically evaluated experimental vapor pressure data sets supplemented with calculated data for low temperature range were used in the development of vapor pressure equations.The optimum number of terms, coefficients and exponents of the Wagner-type equation were derived by means of the Setzmann-Wagner program OPTIM based on the combination of the stepwise regression analysis and evolutionary optimization method. Equations were checked by the reduced enthalpy of vaporization criterion derived from Clausius-Clapeyron equation and specific volume of ideal gas. An equation developed using 261 experimental data points and low temperature data calculated by Lüddecke & Magee gives the RMS deviation 0.102 %, second equation based on the same experimental data and data calculated by Tillner-Roth gives the RMS deviation 0.101 % from experimental points. The triple point pressure extrapolated to the measured temperature T_{tp} = 136.34 K is discussed. Comparison with vapor pressure equations by Outcalt & McLinden, Duarte-Garza and Kubota is given as well.

K**EY WORDS:** critical point, difluoromethane, triple point, vapor pressure equation.

1. INTRODUCTION

Vapor pressure of difluoromethane (HFC32) was intensively measured in the temperature range from 149 K to the critical point [1]. More then 20 vapor pressure equations for HFC32 which describe usually the measured range only or correlate a limited number of measured data sets can be found in the literature. Most methods for the measurements in the low pressure region (below approx. 150 kPa) are time-consuming and relatively inaccurate [2]. Recently appeared in the literature estimation procedures which enable to extrapolate high accuracy vapor pressure data down to the triple point [3,4,5]. The aim of our work is the critical evaluation of measured vapor pressure data and with the aid of derived low pressure data by mentioned estimation procedures to describe vapor pressure over the entire temperature range from the triple to the critical point using Wagner-type equation. Obtained results are shortly discussed.

2. CRITICAL EVALUATION OF MEASURED VAPOR PRESSURE DATA

Fourteen experimental vapor pressure data sets [7, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24 and 25] were included in the evaluation process. The two most reliable vapor pressure equations were selected from more than twenty equations and the deviations of particular data and data sets were calculated. Both equations were of the Wagner-type

$$\ln(p/p_c) = (T_c/T)\sum a_i \tau^{n_i} \; ; \qquad \tau = 1-(T/T_c)$$

which enables accurate description of the vapor pressure over the entire temperature range. The first equation with three constants was derived by Kubota [6] for the range

between 208 K and T_c correlating reported data [7,11,12,13,15,] within ± 5 mK. The second one with five constants was derived by Outcalt & McLinden [29] using data by Defibaugh [21], Holcomb [14] and those derived from the saturated heat capacity by Lüddecke & Magee [3]. The RMS deviation between data used for correlation from calculated values is 0.023 %.

For the particular measured points the absolute deviation (Δp) and percentage deviation (δp) were calculated:

$$\Delta p = p_{\exp} - p_{eq} \; ; \qquad \delta p = 100 \Delta p / p_{\exp} \; \%$$

For the particular data sets following statistics were established:

absolute average deviation $AAD = \frac{1}{n} \sum |\delta p_i| \; \%$

systematic deviation $BIAS = \frac{1}{n} \sum \delta p_i \; \%$

standard deviation $SDV = \sqrt{\frac{\sum (\delta p_i - BIAS)^2}{n-1}} \; \%$

root-mean square deviation $RMS = \sqrt{\frac{1}{n} \sum (\delta p_i)^2} \; \%$

The survey of statistical deviations of particular data sets from Kubota and Outcalt & McLinden equations is in Table I.

Measurements [13, 14, 15, 17, 18, 19, 21, 22, 24 and 25] were selected as reliable for the further processing.

3. ESTIMATED VAPOR PRESSURE DATA AT LOW PRESSURES

Lüddecke and Magee [3] derived vapor pressure data at pressures lower than 6.798 kPa from the saturated liquid heat capacity measurements by applying a thermodynamic relationship between saturated liquid heat capacity and the temperature derivatives of the vapor pressure, by a method devised by Baehr [27].

Tillner-Roth´s method [4] involves a nonlinear regression analysis based on the Clausius-Clapeyron equation and a simple relation of the enthalpy of vaporization. He estimated 49 low-pressure data ranging from the T_{tp} to 232 K.

The method by Duarte-Garza and Magee [5] starts from the measured internal energy changes (or calculated from an equation of state or alternatively caloric data may be employed) and reference value of the vapor pressure and its derivative with temperature evaluated near the normal boiling point temperature.

4. DEVELOPMENT OF THE VAPOR PRESSURE EQUATION

The Wagner-Setzmann program OPTIM [26], based on the stepwise regression analysis connected with the evolutionary optimization method was employed for the search after the optimum number of terms, appropriate coefficients and exponents of the Wagner-type vapor pressure equation with critical parameters T_c = 351.26 K and p_c = 5.785 MPa. The investigation started with the maximum number of terms equal 6, the step for exponents n_i was chosen 1/2, but another steps as 1/4 and 1/3 were tested. In parallel with the regression analysis the course of the reduced enthalpy of vaporization derived from Clausius-Clapeyron equation and ideal gas equation of state was checked in the low temperature region up to 180 K.

If the difference between the specific volume of saturated vapor and saturated liquid in the Clausius-Clapeyron equation is replaced by the specific volume of ideal gas, the specific enthalpy of vaporization in the dimensionless form is

$$\frac{\Delta h_{id}}{RT} = T\frac{d\ln(p_s)}{dT}$$

The derivative of vapor pressure was calculated from the tested equation. For calculations based on the data points by Lüddecke & Magee [3] and by Tillner-Roth [4] the previous equation was integrated. In a short temperature range Δh_{id} can be considered as a constant.

Then for the two neighboring data points holds

$$\frac{\Delta h_{id}}{RT_M} = \frac{T_M}{T_2 - T_1}\ln\left(\frac{p_{s2}}{p_{s1}}\right),$$

where the mean temperature is $T_M = \sqrt{T_1 T_2}$.

Application of ideal gas specific volume in the Clausius-Clapeyron equition has small influence on the reduce enthalphy of vaporization in the neighborhood of the triple point. At temperature 140 K the estimated deviation is less than 0.03 %, at 180 K less than 0.6 %. This simplification has the same effect on the reduced Δh_{id} calculated from data points.

5. RESULTS

The experimental data sets [13,14,15,17,18,19,21,22,24 and 25] were finally used in the development of vapor pressure equation supplemented with two data

sets [3] and [4]. There is a considerable difference between data sets [3] and [4], namely at low temperatures. The deviations are given in Table II.

The course of the reduced enthalpy of vaporization differs also very much as is shown in Fig.1. That was the reason to carry out a detailed analysis separately with data sets [3] and [4].

A simple accurate auxiliary equation was developed for data [3]. Very good agreement in the course of the reduced enthalpy of vaporization was reached.The extrapolation gave the triple point pressure p_{tp} = 46.3 Pa at T_{tp} = 136.34 K for data [3].

The vapor pressure equation developed from the experimental data sets mentioned above and data [3] is indicated as equation "A". Its parameters are given in Table III. together with equations by Outcalt and McLinden [29], Duarte-Garza & Magee [5] and Kubota [6]. Statistical deviations for ten selected data sets are included in Table III. as well as the local deviations of several data points by Lüddecke & Magee [3]. These deviations for all data points are shown in Fig.2. The course of the reduced enthalpy of vaporization Δh_{id} /R is presented in Fig.1.

Separate elaboration of the same experimental data sets [13,14,...25] together with the data by Tillner-Roth [4] led to the vapor pressure equation indicated as "B". Its parameters are given in Table IV. including statistical deviations. Deviations from data points [4] are shown in Fig.3 and the course of the reduced enthalpy of vaporization Δh_{id} /R in Fig.1. The maximum deviation from Tillner-Roth data is - 0.25 %.

6.CONCLUSION

Fourteen experimental data sets were elaborated and ten of them were used for the development of the vapor pressure equation. Two low temperature data sets were analyzed separately. Because of a large discrepancy between the data by Lüddecke & Magee [3] and Tillner-Roth [4] two different vapor pressure equations were developed. They are indicated as "A" and "B".

Equation "A" has lower number of terms and lower deviations from experimental data sets than equations by Outcalt and McLinden [29] and Duarte-Garza & Magee [5]. It has much smaller deviations from the data by Lüddecke & Magee [3], especially close to the triple point. The value of the triple point pressure calculated from the equation "A" is 46.3 Pa, which doesn't differ much from the value 46.5 Pa calculated from the equation by Duarte-Garza and Magee [5]. Outcalt & McLinden's equation gives 46.9 Pa.

It is remarkable that deviations of all equations mentioned above have the same sign from the data by Lüddecke and Magee. Judging by deviations of the Outcalt & McLinden's equation these data could be suspected from the systematic deviation. But the deviations of Duarte-Garza and Magee decrease when approaching to the triple point as well as deviations of the equation "A" (Fig. 2).

Equation "B" has also very small deviations both from the experimental data sets and from the data by Tillner-Roth. The triple point pressure published by Tillner-Roth [4] is quite different from the value discussed in the previous paragraph. It is 50.70 Pa. The same value gives the equation "B". Precision of the data by Tillner-Roth

[4] is dependent on the accuracy of the simple one-term equation of the enthalpy of vaporization which he used.

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Table I. Survey of statistical deviations of particular experimental data sets from Kubota and Outcalt & McLinden equations

Ref.	Eq.	1AAD [%]	SDV [%]	BIAS [%]	RMS [%]	No. of points
[7]	Kub..	0.2327	0.2877	0.0148	0.2829	(30) 29[1]
	O.+McL.	0.2309	0.2795	0.0421	0.2778	
[13]	Kub.	0.0360	0.0447	-0.0204	0.0468	9
	O.+McL.	0.0360	0.0423	-0.0098	0.0411	
[14]	Kub.	0.1165	0.1750	0.0582	0.1811	25
	O.+McL.	0.1156	0.1554	0.0880	0.1759	
[15]	Kub.	0.0397	0.0432	0.0231	0.0483	27
	O.+McL.	0.0259	0.0337	0.0006	0.0330	
[16]	Kub.	0.2469	0.2942	0.0287	0.2910	32
	O.+McL.	0.2439	0.2855	0.0410	0.2869	
[17]	Kub.	0.0550	0.0602	0.0441	0.0737	(30) 27
	O.+McL.	0.0552	0.0515	0.0542	0.0741	
[18]	Kub.	0.0601	0.0800	0.0075	0.0796	56
	O.+McL.	0.0660	0.0847	0.0259	0.0878	
[19]	Kub.	0.0317	0.0455	-0.0003	0.0442	17
	O.+McL.	0.0184	0.0474	0.0120	0.0475	
[20]	Kub.	0.3855	0.5054	-0.2622	0.5603	25
	O.+McL.	0.3741	0.5093	-0.2579	0.5617	
[21]	Kub.	0.0279	0.0286	-0.0171	0.0326	18
	O.+McL.	0.0065	0.0092	-0.0013	0.0090	
[22]	Kub.	0.0235	0.0240	0.0169	0.0289	(21) 18
	O.+McL.	0.0349	0.0170	0.0348	0.0386	
[23]	Kub.	0.1831	0.2001	0.1338	0.2301	8
	O.+McL.	0.1937	0.2084	0.1486	0.2451	
[24]	Kub.	0.1033	0.0415	-0.1033	0.1102	7
	O.+McL.	0.0923	0.0361	-0.0923	0.0981	
[25]	Kub.	0.1010	0.1248	-0.0872	0.1543	57
	O.+McL.	0.0952	0.1304	-0.0680	0.1461	

[1] points with $T>T_c$ = 351.255 K were omitted

Table II. Deviations between saturation pressures at low temperatures.

T/K	$p_{s[}$ [3]	p_s [4]	Δp_s (Pa)	δp_s (%)
140	81.0	87.5	-6.5	-8.02
150	319.0	334.6	-15.6	-4.89
160	1026.0	1061.0	-35.0	-3.41
170	2818.0	2887.2	-69.2	-2.45
180	6798.0	6926.3	-128.3	-1.88

Table III. The Parameters of Vapor Pressure Equations "A", by Outcalt & McLinden [29], Duarte-Garza & Magee [5] and Kubota [6].

	Eq. „A" This work	Outcalt McLinden [29]	D.-Garza & Magee [5]	Kubota [6]
a_1	-7.53814480	-7.559554	-7.566935	-7.433405
a_2	2.35886776	2.465252	2.484133	1.522618
a_3	-1.88421329	-1.976887	-1.984020	-2.902286
a_4	-3.34123534	-2.021284	-2.067412	0
a_5	0	-1.941251	-1.921275	0
n_1	1	1	1	1
n_2	1.5	1.5	1.5	1.5
n_3	2	2	2	2
n_4	4.5	6	6	-
n_5	-	6.5	6.5	-
T_c/K	351.26	351.35	351.35	351.225
p_c/MPa	5.785	5.795	5.795	5.780
T_{nbp}/K	221.484	221.491	221.500	221.500
p_{tp}/Pa	46.3	46.9	46.5	-
Statistic deviations from experimental data				
AAD %	0.0629	0.0624	0.0708	0.0666
BIAS %	-0.00177	-0.00595	0.02816	-0.00775
SDV %	0.1018	0.1027	0.1045	0.1056
RMS %	0.1016	0.1027	0.1080	0.1057
Percentage deviations from data by Lüddecke & Magee [3]				
T/K 140	-0.106	-1.397	-0.506	-
160	-0.498	-1.404	-0.911	-
180	-1.011	-1.425	-1.170	-
Band of percentage deviations from data [15,. 19] up to 240 K				

from	-0.071	-0.082	-0.0	-0.06
to	0.070	0.055	0.135	0.09

Table IV. Parameters of Equation “B“

a_1	-7.52623115	n_1	1	AAD %	0.0600
a_2	2.25589183	n_2	1.5	BIAS %	-0.00436
a_3	-1.66291028	n_3	2	SDV %	0.1009
a_4	-2.65474971	n_4	4	RMS %	0.1008

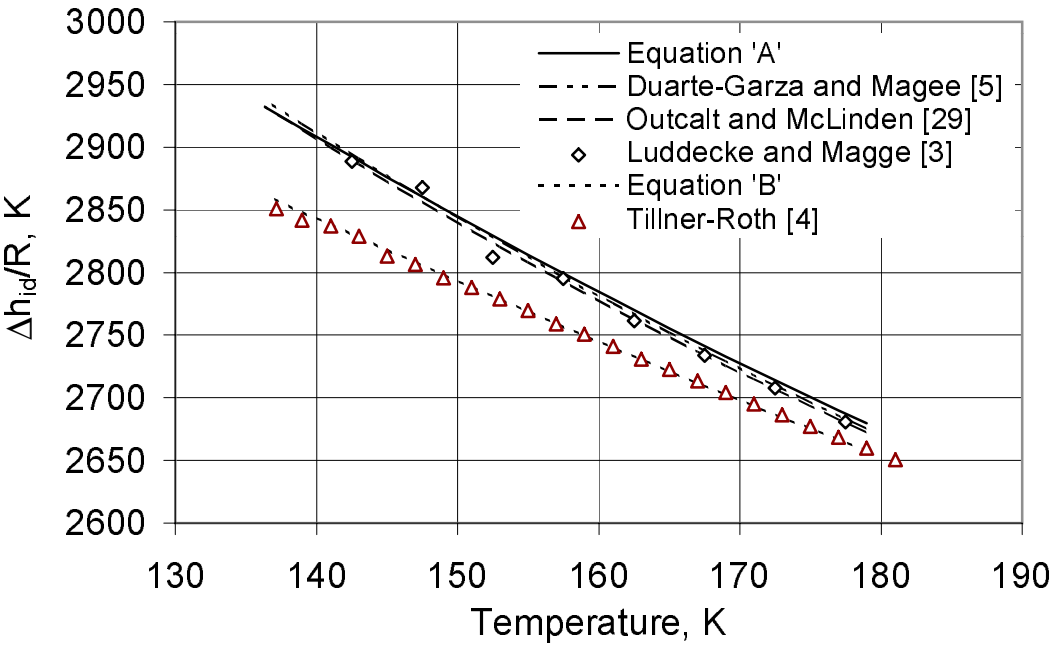
T_c = 351.26 K; p_c = 5.785 MPa; T_{nbp} = 221.488 K; p_{tp} = 50.70 Pa

FIGURE CAPTIONS

Fig. 1. Reduced enthalpy of vaporization.

Fig. 2. Vapor-pressure comparisons: baseline, data by Lüddecke and Magee [3].

Fig. 3. Vapor-pressure comparisons: baseline, data by Tillner-Roth [4].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2800
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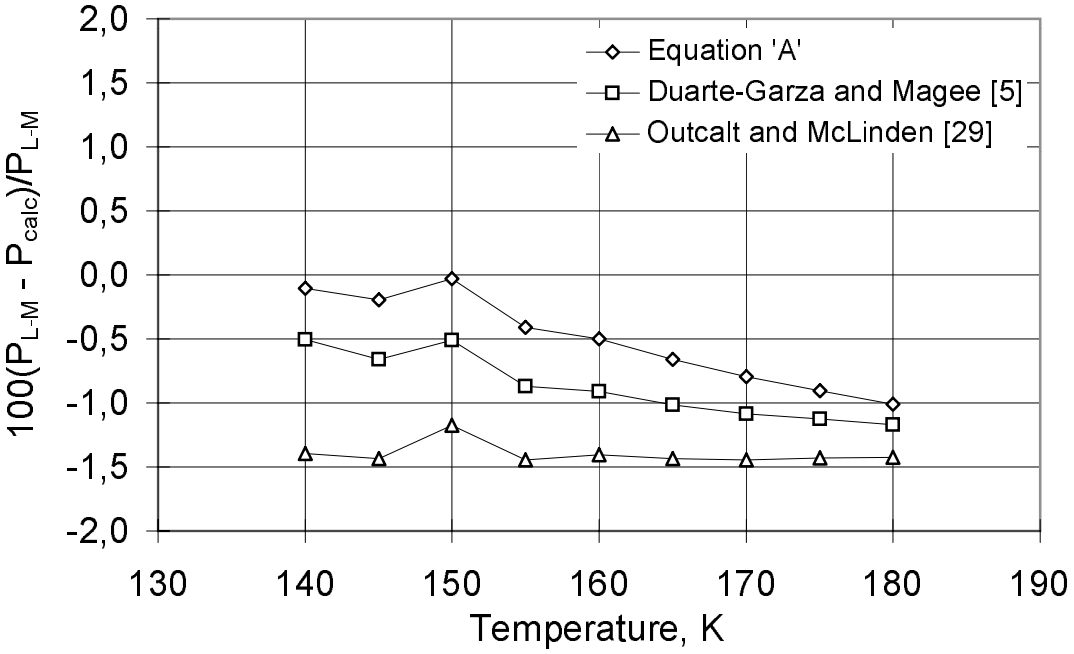
$\Delta h_{id}/R$, K
130
140
150
160
170
180
190
Temperature, K
Equation 'A'
Duarte-Garza and Magee [5]
Outcalt and McLinden [29]
Luddecke and Magge [3]
Equation 'B'
Tillner-Roth [4]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100(P_L-M - P_calc)/P_L-M
130
140
150
160
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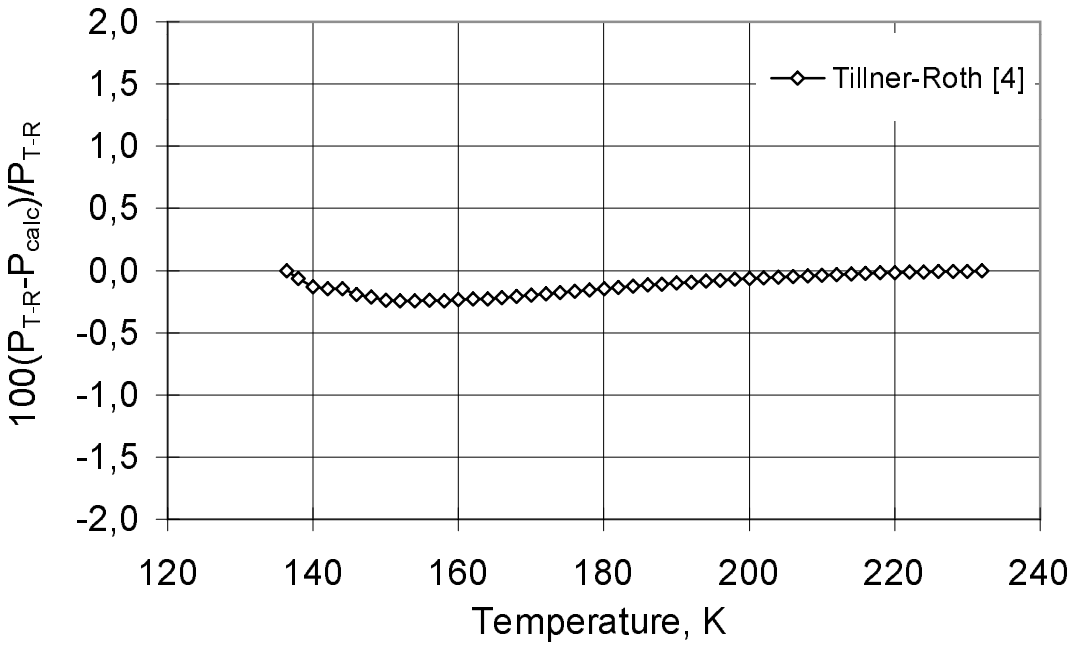
180
190
Temperature, K
Equation 'A'
Duarte-Garza and Magee [5]
Outcalt and McLinden [29]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100(P_T-R-P_calc)/P_T-R
Tillner-Roth [4]
120
140
160
180
200
220
240
Temperature, K