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THERMODYNAMIC PROPERTIES OF R23/116 AZEOTROPIC MIXTURE

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ABSTRACT

New measurements of critical parameters, saturated vapor pressure, saturated-liquid and saturated-vapor densities, and PVT-data for the superheated vapors of the R23/116 azeotropic mixture (46/54 mass percent) are presented. Saturated vapor pressure, saturated-liquid and saturated-vapor densities were measured over a temperature range from -40 to 10°C. PVT data for the superheated vapors were obtained on the isotherms and on the isochores by two independent experimental procedures over a temperature range from 10 to 60°C and a pressure range from 800 to 7350 kPa. The obtained results have been used for developing coefficients for a modified Martin-Hou equation of state and calculating the thermodynamic properties.

NOMENCLATURE

C_p^o	ideal gas heat capacity at P = Const
C_v^o	ideal gas heat capacity at V = Const
d	density
d_c	critical density
H_l	saturated liquid enthalpy
H_v	vapor enthalpy
P	pressure
P_c	critical pressure
P_r	P/P_c, reduced pressure
R	gas constant
S_l	saturated liquid entropy
S_v	vapor entropy
T	temperature
T_b	boiling point at atmospheric pressure
T_c	critical temperature
T_r	T/T_c, reduced temperature
V	specific volume
μ	molecular mass

INTRODUCTION

A family of new pure and mixed refrigerants is currently under consideration as long-term alternatives for low-temperature refrigeration. The azeotropic mixture of the refrigerants R23/116 (46/54 mass %) has been introduced as an alternative to R503. The R23/116 mixture has the proposed ASHRAE number R508B,

The successful application of this mixture as working fluid for low-temperature refrigerating systems requires reliable thermodynamic properties over a range of parameters including the saturated liquid and vapor and the single-phase vapor region. In this paper, we present new measurements of critical parameters, saturated vapor pressure, saturated-liquid and saturated-vapor densities, and PVT-data for the superheated vapors. A modified Martin-Hou equation of state and coefficients for calculating thermodynamic properties are also presented.

EXPERIMENTAL PROCEDURE AND RESULTS

Critical Parameters

A special high pressure sapphire visual cell was used for measuring the critical parameters. The cell was installed inside the view temperature bath which provided precision temperature control (to ± 0.002 °C). Near the critical point the experiments were performed with the temperature step of 0.005 °C. The critical point was determined by observing disappearance of the fluid meniscus. The uncertainties of critical temperature, pressure, and density measurements are estimated to be ± 0.1 °C, ± 5 kPa, and ± 2 kg/m^3, respectively.

Saturated Properties

Saturated vapor pressures were determined by direct pressure measurements using stainless steel cell and precision pressure transducer. The uncertainty of the saturated vapor pressure measurements is estimated to be ± 0.1 %.

Saturated-liquid and saturated-vapor densities were measured using cells constructed of stainless steel cylinder with volume of 180 cm^3 and the sapphire visual tube. The sapphire tube was attached to the top of the stainless steel cylinder for measurements of saturated-liquid densities and to the bottom of this cylinder for measurements of saturated-vapor densities. In both cases, the visual tube allowed us to determine the level of phase equilibrium within the system and the volume of the system occupied by the certain phase. The uncertainties of the saturated-liquid and saturated-vapor density measurements are estimated to be ± 0.2 % and ± 0.5 %, respectively.

Saturated properties of R508B are given in Table 1.

PVT Measurements

PVT-experiments for the superheated vapors were performed using two independent procedures: constant-volume method for measurements along the isochores and constant-temperature method for measurements along the isotherms. For both of them gravimetric determination of the amount of mixture under investigation was applied. The uncertainty of the temperature is ± 0.02 °C, and for pressure it is less than ± 0.05 %. The principal source of uncertainty is the cell volume which has an estimated statistical uncertainty of ± 0.005 % and estimated systematic uncertainty of ± 0.025 %. Overall, the uncertainty of the density values is estimated to be less than ± 0.2 %. More detailed description of the experimental apparatus and procedure is given in our previous publication [1].

The results of PVT-measurements on the isotherms (I series) and on the isochores (II series) are given in Tables 2 and 3, respectively. In the II series, the measurements were done in the singe-phase region, and also in the two-phase region (vapor pressure data) for each isochore. Comparisons of the experimental PVT-data from two independent experimental series (Table 4) show that they are in good agreement.

Two values of the saturated-vapor density were found by extrapolation of the experimental isochores to the saturation line. Comparisons of the saturated-vapor densities obtained by direct measurements and by extrapolation of the experimental isochores show that deviations are equal to 1.4 % and 1.1 %, respectively.

Table 1. Saturated properties of R508B

T (°C)	P (kPa)	T (°C)	d_{liq} (kg/m³)	T (°C)	d_{vap} (kg/m³)
-41.08	816.9	-40.02	1316.1	-39.92	50.93
-40.00	846.0	-30.00	1250.3	-30.03	71.72
-31.14	1145.5	-25.02	1213.8	-25.01	85.30
-25.12	1386.3	-20.01	1175.5	-20.00	100.28
-20.01	1622.8	-14.99	1131.9	-15.03	119.32
-15.00	1871.1	-9.98	1084.4	-9.99	140.39
-9.97	2156.6	-4.99	1030.0	-5.00	167.04
-5.03	2465.7	0.03	969.1	0.01	199.40
0.01	2807.9	5.00	889.5	5.00	237.6
4.43	3146.8	9.99	781.2	10.02	304.3
8.07	3443.1				
10.01	3619.6				
12.20	3831.1				

Table 2. PVT data of R508B (I series)

T (°C)	P (kPa)	d (kg/m³)	T (°C)	P (kPa)	d (kg/m³)
10.00	816.6	35.84	10.00	3320.8	235.17
20.00	850.9	35.84	20.00	3655.4	235.16
30.00	885.2	35.83	30.00	3977.0	235.15
40.00	925.2	35.83	40.00	4298.6	235.15
50.00	958.4	35.83	50.00	4611.5	235.14
60.00	987.0	35.82	60.00	4915.7	235.13
10.00	1268.7	58.80	30.00	4645.7	316.47
20.00	1329.1	58.80	40.00	5103.1	316.46
30.00	1382.6	58.79	50.00	5556.9	316.45
40.00	1440.3	58.79	60.00	6003.4	316.44
50.00	1502.0	58.79	30.00	5275.8	420.40
60.00	1561.0	58.78	40.00	5909.8	420.39
10.00	1961.9	100.49	50.00	6533.7	420.38
20.00	2076.3	100.49	60.00	7152.7	420.37
30.00	2186.1	100.48	30.00	5767.1	526.69
40.00	2291.8	100.48	40.00	6570.0	526.67
50.00	2401.0	100.48	50.00	7359.1	526.65
60.00	2513.2	100.47			
10.00	2757.0	162.02			
20.00	2962.2	164.01			
30.00	3170.3	164.00			
40.00	3372.5	164.00			
50.00	3565.8	163.99			
60.00	3759.1	163.99			

Table 3. PVT measurements of R508B (II series)

T (°C)	Pressure (kPa)		
	Saturated Pressure	Isochore #1 $d = 219.82 \pm 0.05$ kg/m^3	Isochore #2 $d = 146.12 \pm 0.05$ kg/m^3
-16.00	1826.1		
-13.09	1989.3		
-10.77	2113.9		
-6.14			2277.2
-2.55	2638.8		
0.00			2386.0
0.32	2835.0		
1.24	2904.2		
3.16		3008.0	
5.00		3060.8	
10.00		3223.4	2563.6
20.00		3532.5	2745.1
30.00		3826.7	2914.2
40.00		4111.0	3085.2
50.00		4390.6	3245.5

Table 4. Comparisons of PVT data

T (°C)	Pressure (kPa)			
	Isochore $d = 219.82$ kg/m^3		Isochore $d = 146.12$ kg/m^3	
	I series	II series	I series	II series
10	3219	3223	2557	2564
20	3525	3533	2740	2745
30	3823	3827	2919	2914
40	4115	4111	3090	3085
50	4403	4391	3262	3246

MODEL AND CORRELATIONS

The data in this paper have been used to develop correlations for the present binary system. Often, in refrigerant applications, the Martin-Hou equation of state with auxiliary functions [2] is used for practical calculations. The following correlations based on the modified Martin-Hou model are given for R508B.

Equation of State (Martin-Hou EOS)

$$P = \frac{RT}{V-b} + \sum_{i=2}^{5} \frac{A_i + B_i T + C_i \exp(-kT/T_c)}{(V-b)^i} \tag{1}$$

$A_2 = -9.859954 \cdot 10^{-2}$ $B_2 = 1.329512 \cdot 10^{-4}$ $C_2 = -2.750786 \cdot 10^{0}$

$A_3 = 1.943104 \cdot 10^{-4}$ $B_3 = -3.673400 \cdot 10^{-7}$ $C_3 = 8.136346 \cdot 10^{3}$

$A_4 = -2.415544 \cdot 10^{-7}$ $B_4 = 6.399736 \cdot 10^{-10}$ $C_4 = -3.173366 \cdot 10^{-5}$

$A_5 = 1.741779 \cdot 10^{-10}$ $B_5 = -5.966795 \cdot 10^{-13}$ $C_5 = 3.819294 \cdot 10^{-8}$

$R = 8.716059 \cdot 10^{-2}$ $b = 4.309291 \cdot 10^{-4}$ $k = 6.25;$

(P in kPa, T in K, V in m^3/kg, $P_c = 3926$ kPa, $T_c = 287.14$ K, $d_c = 586.2$ kg/m^3, $\mu = 95.393$, and $T_b = 184.88$ K).

Saturated Liquid Pressure (Bubble Point Pressure)

$$\ln(P/P_c) = \frac{1}{T_r}\left(A + BX + CX^2 + DX^3 + EX^4 + FX^5\right) \tag{2}$$

$A = -1.41801$ $B = -6.57620$ $C = -0.27991$ $D = -1.45324$

$E = -0.06623$ $F = -2.91797$ $X = (1-T_r) - X_0$ $X_0 = 0.215245$

Saturated Vapor Pressure (Dew Point Pressure)

$$\ln(P/P_c) = \frac{1}{T_r}\left(A + BX + CX^2 + DX^3 + EX^4 + FX^5\right) \tag{3}$$

$A = -1.41842$ $B = -6.59163$ $C = -0.612030$ $D = 4.21582$

$E = -11.27539$ $F = -21.9375$ $X = (1 - T_r) - X_0$ $X_0 = 0.215245$

Saturated Liquid Density

$$d/d_c = A + Bx + Cx^2 + Dx^3 + Ex^4 \tag{4}$$

$A = 1.0$ $B = -0.1670326$ $C = 7.885847$

$D = -9.550139$ $E = 4.713835$ $x = (1 - T_r)^{1/3}$

Ideal Gas Heat Capacity

$$C_p^0 = A + BT + CT^2 + DT^3 \tag{5}$$

$A = 1.5852536 \cdot 10^{-1}$ $B = 2.5441972 \cdot 10^{-3}$ $C = -2.028597 \cdot 10^{-6}$ $D = 5.7703343 \cdot 10^{-10}$

(C_p in kJ/kg·K, T in K, and $C_v^0 = C_p^0 - 0.087161$).

Saturated Liquid Enthalpy

$$H_l = A + BX + CX^2 + DX^3 + EX^4 + FX^5 \tag{6}$$

$A = 141.066$ $B = -356.266$ $C = -349.375$ $D = 404.813$

$E = 2480.00$ $F = 2480.00$ $X = (1 - T_r)^{1/3} - X_0$

(H_l in kJ/kg, T in K, and $X_0 = 0.573528$)

Vapor Enthalpy

$$H_v = AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^2}{4} + PV + \left[\frac{A_2}{V-b} + \frac{A_3}{2(V-b)^2} + \frac{A_4}{3(V-b)^3} + \frac{A_5}{4(V-b)^4} \right]$$

$$+ e^{-kT/T_c} \left(1 + \frac{kT}{T_c}\right) \left[\frac{C_2}{V-b} + \frac{C_3}{2(V-b)^2} + \frac{C_4}{3(V-b)^3} + \frac{C_5}{4(V-b)^4} \right] + X \tag{7}$$

$A = 7.136477 \cdot 10^{-2}$ $B = 2.544197 \cdot 10^{-3}$ $C = -2.028597 \cdot 10^{-6}$ $D = 5.770334 \cdot 10^{-10}$

(All other constants are same as in Eq. (1), H_v in kJ/kg, T in K, P in kPa, V in m^3/kg, and $X = 186.059$).

Vapor Entropy

$$S_v = A\ln(T) + BT + \frac{CT^2}{2} + \frac{DT^3}{3} + R\ln(V-b) - \left[\frac{B_2}{V-b} + \frac{B_3}{2(V-b)^2} + \frac{B_4}{3(V-b)^3} + \frac{B_5}{4(V-b)^4} \right]$$

$$+ \frac{k e^{-kT/T_c}}{T_c} \left[\frac{C_2}{V-b} + \frac{C_3}{2(V-b)^2} + \frac{C_4}{3(V-b)^3} + \frac{C_5}{4(V-b)^4} \right] + Y \tag{8}$$

$A = 7.136477 \cdot 10^{-2}$ $B = 2.544197 \cdot 10^{-3}$ $C = -2.028597 \cdot 10^{-6}$ $D = 5.770334 \cdot 10^{-10}$

(All other constants are same as in Eq. (1), S_v in kJ/kg·K, T in K, V in m^3/kg, and $Y = 0.77028$).

Saturated Liquid Entropy

$$S_l = S_v - \frac{H_v - H_l}{T} \tag{9}$$

(H_l, H_v in kJ/kg, S_l, S_v in kJ/kg·K, and T in K).

CONCLUSION

New thermodynamic property measurements of R23/116 mixture (R508B) including critical parameters, saturated vapor pressure, saturated-liquid and saturated-vapor densities, and PVT-data for the superheated vapors are presented. These results have been used to develop coefficients for a modified Martin-Hou equation of state and thermodynamic property calculations.

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