An Experimental Study of the Thermodynamic Properties of the Binary Refrigerant Mixture R32-R134A[1]

O.V. Beliajeva[2] , A.J. Grebenkov[2,3], N.F. Levchouk[2] , B.D. Timofejev[2]

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[2] Institute of Power Engineering Problems, Academy of Sciences, Sosny, 220109 Minsk, Belarus.

[3] Author to whom correspondence should be addressed.

ABSTRACT

Volumetric behaviour of the refrigerant binary mixture of HFC32 (R32) in HFC134A (R134A) have been studied by the method of the variable volume piezometer. Density was measured in the temperature range of 250-320K at pressure of 1.5-2.5 MPa along with fixing the dew and bubble points on a phase transition curve. The data were completed up to temperature of 340K with the results of measurement of the bubble point pressure in the constant volume piezometer. The estimated experimental error is 0.2% and 0.4% for density data and pressure measurements correspondingly.

To describe the volumetric behaviour for the entire interval of composition the Tait equation of state has been used. The Redlich-Kister correlation was used to define the deviations from density additive value. The standard error of approximation was 0.24%.

KEY WORDS: density; equation of state; experimental method; refrigerant; vapour-liquid equilibrium.

1. INTRODUCTION

The thermophysical properties of HFCs and FCs which are promising substitutes for the refrigerants based on CFCs are at present under the intensive study. The present paper deals with experimental study of refrigerant based on mixture of R134A and R32. The results obtained on volumetric behaviour are described below.

2. METHOD AND APPARATUS

The methods of variable-volume and constant-volume piezometer were used to measure density and phase equilibrium parameters of four binary compositions of the mixture R32+R134A.

The technological scheme of the variable-volume apparatus is presented in Fig. 1. The experimental cell consists of cylindrical tube of 200 mm length made of molybdenum glass. The internal diameter of the cell is 4.8 mm. The tube is placed inside the stainless steel vessel. Mercury is used as a medium to change the volume of cell and to transmit the pressure from the investigated fluid to a tensor pressure detector and a piston manometer. In order to reduce time needed to reach thermodynamic equilibrium the cell is supplied with a magnetic mixer. The height of mercury is measured visually with horizontal microscope to determine the volume (V) of investigated fluid. The relation between the mercury meniscus location and the volume of fluid is determined by calibration. Corrections to this dependence take into account meniscus curvature, capillary depression, thermal extension and deformation of the cell volume with pressure.

The experimental cell is placed in the isolated ethanol bath controlled with electronic scheme and resistance thermometer. Temperature variations within the cell do not exceed

0.01 K during the measurement period. Pressure is measured with tensor detector calibrated with piston manometer, and temperature is measured with platinum resistance thermometer. The bubble point pressure is determined when vapour is first observed in the experimental cell. At this time the position of the mercury meniscus is determined and the liquid density (r) is evaluated. The dew point pressure is identified as a point of deformation of the *P*-*T*-curve.

The constant-volume piezometer has volume of 40 cm^3, and it is placed in the thermostat of the apparatus used for acoustic measurement [1]. Pressure at the bubble point is measured with tensor detector.

The calibration of the variable-volume piezometer was carried out prior to main experiments. The volume occupied by medium investigated is determined with account of corrections caused by pressure and temperature:

$$\rho = G\{(H_0 - H_k)\, V_0\, [1 + \alpha_v\, (T_n - T_k) + \beta_T\, (p - 0.1)]\}^{-1}\,, \qquad (1)$$

where ρ — density of fluid, G — mass of fluid loaded, H_0 — meniscus level while full load of piezometer, H_k — current meniscus level, V_0 — volume of the piezometer at normal condition per height unit, α_v — volumetric coefficient of thermal extension, β_T — isothermal coefficient of extension, T_n and T_k — temperature inside of the piezometer and indoor temperature, p — pressure in the piezometer.

The values of V_0, H_0 , α_v and β_T in Eq. (1) were found by non-linear regression method on a basis of calibration of the piezometer with R134A as a standard fluid [2, 3]. The deviation of calibration data from standard ones [2, 3] is 0.04%. Three control

measurements of density of R32 were carried out at indoor temperature. The deviations from data presented in [4] are 0.04, 0.07 and 0.22 %.

The uncertainty of phase equilibrium parameters measured is estimated to be 0.02K for temperature (T) and 0.15% for pressure (p). Density (ρ) of refrigerants in liquid phase is measured with standard error of 0.35%. Each composition of mixture is determined with a standard error of about 0.001 weight fraction.

3. EXPERIMENTAL DATA

The pressure-composition and density-composition relations of investigated along the saturated vapour/liquid curve were measured in a temperature range from 250K to 320K. Four compositions of the R32+R134A mixture and its components were studied. The experiment was carried out at a constant temperature, while the pressure in the cell was measured as a function of the cell volume. The p-ρ parameters were fixed and isotherms $p(\rho)_{T=const}$ were plotted for each fluid.

The vapour pressure values obtained for the pure components (R32 and R134A) are in a good agreement with reference data available in literature. The deviation does not exceed the sum of standard errors. The values of pressure at the dew and bubble points are given in Tables I, II and III. Experimental data on density obtained are presented in Table IV.

4. RESULT AND DISCUSSION

4.1. Phase equilibrium parameters.

The experimental data on the parameters of boiling curve were approximated with use of model [5]. For saturation parameters of the basic component (R32) the Wagner correlation [6] is applied. The pressure at the saturation curve of R134A is described with a

help of additional coefficients φ_i and θ_i incorporated into the same equation. As a result, the saturated vapour pressure values of these refrigerants with standard error of less than 3 kPa are defined by the following equation:

$$\ln(p_i/\varphi_i p_{ci}) = [1/(1-\tau_i)](A\tau_i^{\alpha} + B\,\tau_i^{\beta} + C\,\tau_i^{\gamma}), \qquad (2)$$

where $\tau_i = 1 - T/\theta_i T_{ci}$. For the basic component (R32) the constants of Eq. (2) are:

α=1; β=1.5; γ=3; A= -7,43341; B=1.52262; C= -2.90229.

The critical parameters of the components T_{ci}, p_{ci} [6] and the constants of Wagner's equation used in calculation in accordance with Eq. (2), and the correlation coefficients φ_i and θ_i for R134A are given in Tables V and VI.

The boiling pressure data of the refrigerant mixtures (p_m) are approximated with the following system of equations in accordance with the model:

$$\ln(p_m/p_{cm}) = [1/(1-\tau_m)](A\tau_m + B\,\tau_m^{1.5} + C\,\tau_m^{3}) \;, \quad \tau_m = 1 - T/T_{cm}\,, \qquad (3)$$

The pseudo critical parameters for mixture p_{cm} and T_{cm} are calculated according to the empirical correlation:

$$T_{cm} = x_1\,\theta_1 T_{c1} + \theta_2 T_{c2}\;, \qquad (4)$$

$$p_{cm} = x_1^2\,\varphi_1 p_{c1} + 2\,x_1 x_2 (1-k_{12})[\varphi_1 p_{c1}\varphi_2 p_{c2}]^{0,5} + x_2^2\,\varphi_2 p_{c2}\,, \qquad (5)$$

where x_1 and x_2 — mole fraction of the components R134A and R32. The correlation of k_{12} coefficient *versus* temperature and composition is used in a form of:

$$k_{12} = k_{12}^0 + k_{12}^1 (T - T_{12}^0) + m_{12}(x_1 - x_2)\;. \qquad (6)$$

Here is k_{12}^0, k_{12}^1, T_{12}^0 and m_{12} — fitting parameters defined by non-linear regression method on a basis of all data measured.

The standard deviation between the experimental pressure data and calculated ones while using Eqs. (2-6) is 0.30% and 0.43% for boiling curve and condensation curve correspondingly. The parameters of Eqs. (2-6) are given in Table V. In Fig. 2 the results of calculation for two isotherms are plotted.

The bubble point data for mixture R32+R134A have been also received in [7] in the temperature range of 283K-313K and composition interval of 0.12-0.67 mole fraction. We approximated these data with the above model. The disagreement between our correlation and the results of [7] does not exceed the standard deviation of the last.

4.2. Density in liquid phase

The Tait equation [7] was used to describe the experimental values of density of each component of the mixture R32+R134A:

$$1/\rho=(1/\rho_S)\{1 - A \ln[(B+p)/(B+p_S)]\}, \qquad B = \sum_{j=0}^{2} B_j \tau^j \quad , \tag{7}$$

where $\tau=1-T/T_C$ is relative temperature, p_S is vapour pressure, and density on saturated curve (ρ_S) of R134A and R32 refrigerants is defined by the following expression:

$$\rho_S = \rho_C(1 + R_1 \tau^{0.38} + R_2 \tau^{1.6}), \tag{8}$$

In Table VI the range of applicable parameters along with a number of experimental values, standard deviation, critical parameters and the constants of Eqs. (7)-(8). Eq. (7) was used also to approximate the data on density of mixture R32+R134A where specific volume of the mixture at boiling curve parameters (V_{sm}) *versus* composition of mixture and temperature is expressed with the following form:

$$V_{sm}=(1/\rho_{sm})= x_1 V_{s1}+x_2 V_{s2}+ \Delta V^E. \quad (9)$$

In Eq. (9) the excess mole volume ΔV^E is calculated with Reidlich-Kister correlation:

$$\Delta V^E = x_1 x_2 \sum_{i=0}^{2} \sum_{j=0}^{2} A_{ij} T^i (x_1 - x_2)^j . \quad (10)$$

The maximum difference from the additive values is 4%. The dependence of B parameter of the Tait equation on the mixture composition is assigned in polynomial form:

$$B_m = \sum x_i B_i + x_1 x_2 \sum_{i=0}^{1} K_i (x_1 - x_2)^i , \quad (11)$$

where pseudo critical temperature of mixture is calculated according Y. Higashi [7]:

$$T_{cm}= \theta_1 T_{c1} + \theta_2 T_{c2} - 2.78\, \theta_1 \theta_2 , \quad (12)$$

$$\theta_i = x_i V_{ci}^{2/3} \left(\sum x_j V_{cj}^{2/3}\right)^{-1} . \quad (13)$$

As a result, the density of mixture is defined with the following equation:

$$\rho_m =\rho_{sm}\{1 - 0{,}087 \ln[(B_m+p)/(B_m+p_{sm})]\}^{-1} . \quad (14)$$

In Eq. (14) the value p_{sm} is pressure at the bubble point of mixture. In Eqs. (10) and (11) the coefficients A_{ij} and K_i were evaluated by non-linear regression method with standard deviation of 0.24%. Their values are given in Table VII. The Eqs. (7)-(14) define density of the mixture R32+R134A within temperature range of T=240-320K and pressure up to 6 MPa.

5. CONCLUSION

This study will help in effective choice of alternative refrigerants and will provide the data needed for the design and manufacture of apparatus and techniques for industrial

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Table I. Bubble Point Pressure of Mixture of R32 in R134A

(Method of Variable-Volume Piezometer)

T, K	*p,* MPa	*T,* K	*p,* MPa	*T,* K	*p,* MPa	*T,* K	*p,* MPa
24.4% mol. R32		295,39	0,9090	312,43	1,4291	317.34	2.1137
297.75	0.8800	295,39	0.9087	312,43	1,4297	317.37	2.1125
302.26	0.9968	295,36	0,9095	312,42	1,4289	*91.0 % mol. R32*	
312.64	1.3081	295,35	0,9095	*65.3 % mol. R32*		246.85	0.2970
34.4% mol. R32		295,35	0,9094	262.55	0.4345	253.05	0.3780
255.95	0.2451	295,33	0,9087	282.25	0.8242	271.50	0.7277
283.35	0.6367	295,34	0,9092	282.23	0.8258	290.89	1.2928
295,34	0,9072	302,11	1,0931	289.76	1.0299	290.86	1.2988
295,35	0,9080	302,14	1,0946	289.75	1.0286	297.50	1.5484
295,36	0,9082	302,08	1,0950	297.46	1.2744	297.11	1.5513
295,39	0,9142	302,13	1,0971	297.45	1.2838	302.37	1.7673
295,39	0,9146	302,13	1,0965	307.53	1.6582	317.42	2.5572
295,39	0,9145	302,09	1,0956	307.52	1.6663		
295,38	0,9082	312,41	1,4274	317.33	2.1129		

Table II. Dew Point Pressure of Mixture of R32 in R134A

(Method of Variable-Volume Piezometer)

T, K	*p*, MPa	*T*, K	*p*, MPa	*T*, K	*p*, MPa
24.4% mol. R32		*57.7% mol. R32*		*74.0% mol. R32*	
291.15	0.638	288.35	0.757	287.06	0.848
297.33	0.770	297.37	0.9865	297.34	1.156
306.90	1.006	307.16	1.297	307.29	1.534
307.13	1.016	307.14	1.296	317.07	1.970
317.12	1.325	317.13	1.692	*88.0% mol. R32*	
317.32	1.319			287.29	1.049

Table III. Bubble Point Pressure of Mixture of R32 in R134A

(Method of Constant-Volume Piezometer)

T, K	*p,* MPa	*T,* K	*p,* MPa	*T,* K	*p,* MPa
34,4 % mol. R32		327,59	2,067	315,90	1,519
295,68	0,9226	336,22	2,503	322,51	1,774
306,25	1,228	*31,4 % mol. R32*		327,60	1,999
315,19	1,568	295,66	0,8884	336,23	2,429
295,69	0,9239	306,25	1,186	*91,0 % mol. R32*	
306,27	1,229	306,31	1,187	288,79	1,2198
315,91	1,569	315,90	1,518	295,69	1,4739
322,51	1,835	315,90	1,517		

Table IV. Experimental Data on Density of Mixture of R32 in R134A

T, K	*p*, MPa	ρ , kg m^{-3}	*T* , K	*p*, MPa	ρ , kg m^{-3}
34.4 % mol. R32			*65.3% mol. R32*		
295.39	1.6314	1185.3	282.18	2.4141	1139.5
295.39	2.3480	1.889.5	256.75	1.6733	1237.1
302.03	1.5141	1158.1	256.65	2.3786	1239.2
302.01	2.4389	1162.7	262.75	1.7137	1215.1
312.43	2.0157	1113.0	262.85	2.4743	1218.7
312.43	2.4210	1116.8	271.85	2.2912	1186.8
312.43	2.4346	1116.8	272.05	2.6249	1188.5
255.65	1.9375	1352.3	283.23	2.2232	1141.8
65.3% mol. R32			317.39	2.4324	987.3
289.84	2.066	1113.9	*91.0 % mol. R32*		
297.47	1.875	1074.8	297.53	2.0112	980.3
297.47	2.4676	1083.8	307.58	2.5184	937.6
307.53	2.0695	1030.7	253.4	2.1898	1153.6
307.53	2.6112	1035.3	251.6	2.4923	1153.7
282.24	1.8291	1137.8	254.8	2.4045	1144.3

Table V. Parameters of Eqs. (2)-(6)

Phase	Component	φ_i	θ_i	k_{12}^0	$k_{12}^1 \cdot 10^3$	m_{12}	T_{12}^0
Bubble point	R134a	1,29534	1,03685	-0,76238	2,0607	-0,0255	0
	R32	1	1				
Dew point	R134A	1,29534	1,03685	0.589502	-1.6203	-0.10667	70.263
	R32	1	1				

Table VI. Parameters of the Equation of State

i	**R32** T_C=374.27 K p_C =4.062 MPa ρ_C=424 kg m^{-3} V_C=122 cm^3 mol^{-1}		**R134a** T_C=351.26 K p_C =5.7831 MPa ρ_C=508 kg m^{-3} V_C=201 cm^3 mol^{-1}	
	A = 0.08721		A= 0.08700	
	R_i	B_i	R_i	B_i
0	-	-5.33739	-	-3.95679
1	2.5365	69.1062	2.45342	49.0062
2	0.622957	268.644	0.46143	261.729
Range of temperature and pressure	242-313 P_S - 6 MPa		235-325 P_S - 5 MPa	
Number of data	155		39	
Standard deviation, %	0,0136		0,0132	

Table VII. Parameters of the Eqs. (7)-(14)

i	K_i	A_{ij}		
		j=0	j=1	j=2
0	-23.8701	$-3.2572 \cdot 10^{-2}$	$1.6030 \cdot 10^{-5}$	$-1.7160 \cdot 10^{-5}$
1	1.32402	$9.6910 \cdot 10^{-5}$	$-4.4540 \cdot 10^{-5}$	$-2.0460 \cdot 10^{-5}$
2	0	0	0	$1.6000 \cdot 10^{-7}$

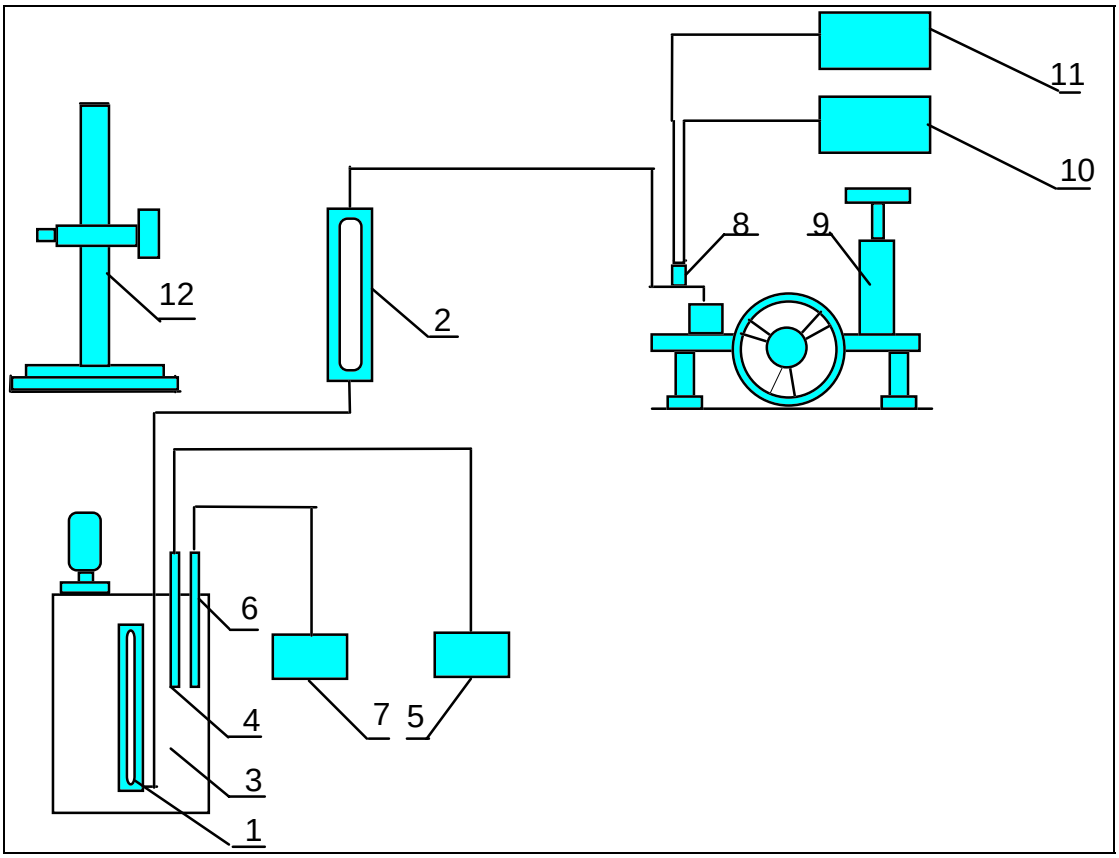

Fig. 1. Scheme of apparatus: 1 - Experimental cell; 2 - Measurement cell; 3 - Thermostat; 4 - Copper resistance thermometer; 5 - Temperature control system; 6 - Platinum resistance thermometer; 7 - Comparator; 8 - Tensor pressure detector; 9 - Piston manometer; 10 - Power supply; 11 - Digital Ω-meter; 12 - Horizontal microscope

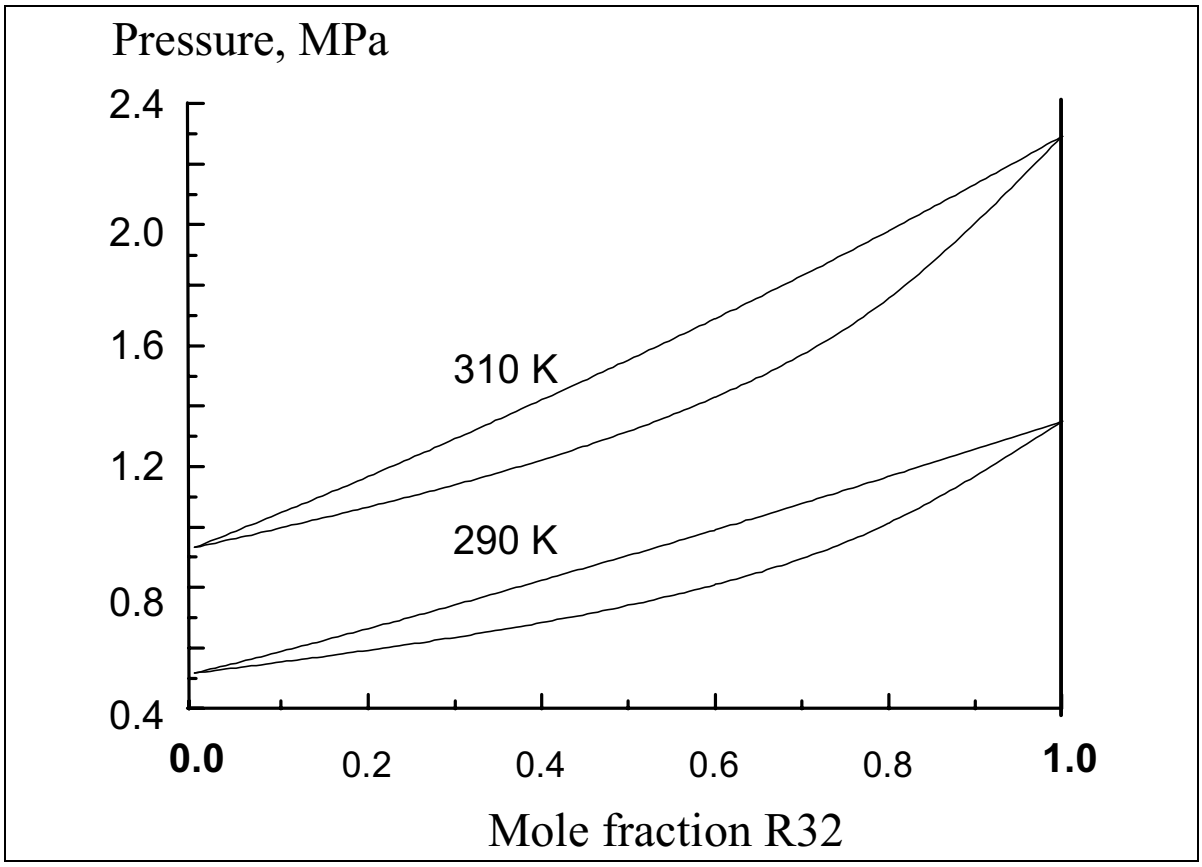

Fig. 2. Vapour-liquid equilibrium for mixture R32+R134A