Vapor pressure, density, and speed of sound of the R134a-R227ea refrigerants in the vapor phase

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Abstract. The pressure on the dew line and density of the gas-phase 69.2 wt.% R134a / 30.8 wt.% R227ea refrigerant were investigated using a constant volume piezometer in the temperature range from 293 to 373 K and at pressures from 0.45 to 3.1 MPa. The speed of sound of the 70.1 wt.% R134a / 29.9 wt.% R227ea mixture (323-373 K, 1.2-1.5 MPa) was also measured using an ultrasonic interferometer. The measurement errors of the temperature, pressure, density, and speed of sound were ±20 mK, ±4 kPa, ± (0.15–0.25)%, and ± (0.2–0.3)%, respectively. Approximation dependences of the studied properties were obtained and their errors were estimated. The obtained results were compared with the calculations using the REFPROP program.

1. Introduction
Currently, the blends of refrigerants are widely used as coolants for refrigerators and heat pump equipment. Despite a number of drawbacks (fractionation), their advantage over individual substances is the possibility to select the composition to optimize the properties of the working fluid for the specific operating conditions of the installations for cold or heat producing. Solving this task requires the availability of the developed methods for predicting the properties of refrigerants depending on the composition and state parameters, as well as reliable experimental data on the thermophysical properties.

The purpose of this work consists in the measurement of the \( p, V, T \)-properties, speed of sound, and pressure on the dew line of blend refrigerants of the R134A-R227ea system in the vapor phase in the previously unstudied composition region, and in determination of the accuracy of their properties description using the program REFPROP [1].

2. Experimental details
The vapor pressure on the dew line and the vapor density of the 69.2 wt.% R134a / 30.8 wt.% R227ea refrigerant in the temperature range from 293 to 373 K and at pressures from 0.45 to 3.1 MPa were investigated by a constant volume piezometer. An ultrasonic interferometer was used for the measurement of the speed of sound in a 70.1 wt.% R134a / 29.9 wt.% R227ea refrigerant (323-373 K, 1.2-1.5 MPa). The temperature \( T \) was measured with standard PTS-10 resistance thermometers, calibrated with an error of 0.02 K. Pressure \( p \) was measured with a quartz manometer, which was previously calibrated with a piston gage. A stainless steel membrane null indicator was used. The measurement errors of the temperature, pressure, density, and speed of sound were ±20 mK, ±4 kPa, ± (0.15–0.25)%, and ± (0.2–0.3)%, respectively [2-4].
The refrigerants of the R134a / R-227ea system were prepared by the gravimetric method with an error of no more than 0.05 wt.%. The initial components (R134a), produced by Forane, France, and (R227ea) produced by Applied Chemistry Research Center, St. Petersburg, had a purity of 99.9% and 99.99%, respectively.

3. Results and Discussion

In Figures 1-2 and in Tables 1-3, the results of the measurements of the refrigerants properties in the vapor phase and on the dew line are shown.

Table 1. Experimental density of the 69.2 wt.% R134a / 30.8 wt.% R227ea refrigerant in the vapor phase.

| $T$ (K) | $p$ (MPa) | $\rho$ (kg m$^{-3}$) | $T$ (K) | $p$ (MPa) | $\rho$ (kg m$^{-3}$) |
|--------|-----------|----------------------|--------|-----------|----------------------|
| 293.15 | 0.4412    | 23.63                | 353.15 | 0.8106    | 35.64                |
| 313.15 | 0.4803    | 23.61                | 353.15 | 1.2991    | 61.79                |
| 313.15 | 0.6900    | 35.71                | 353.15 | 1.8962    | 101.10               |
| 323.15 | 1.1252    | 61.89                | 353.15 | 1.3541    | 61.76                |
| 333.15 | 0.5181    | 23.59                | 353.15 | 1.9998    | 101.05               |
| 333.15 | 0.7513    | 35.67                | 363.15 | 0.5915    | 23.54                |
| 333.15 | 1.1847    | 61.85                | 363.15 | 0.8681    | 35.60                |
| 343.15 | 1.2422    | 61.82                | 373.15 | 1.4083    | 61.73                |
| 343.15 | 1.7891    | 101.15               | 373.15 | 2.1009    | 100.99               |
| 353.15 | 0.5553    | 23.56                |        |           |                      |

Table 2. Experimental vapor pressure of the 69.2 wt.% R134a / 30.8wt.% R227ea refrigerant on dew line.

| $T$ (K) | $p_d$ (MPa) | $T$ (K) | $p_d$ (MPa) |
|--------|-------------|--------|-------------|
| 293.15 | 0.5503      | 343.15 | 2.0211      |
| 313.15 | 0.9745      | 353.15 | 2.5148      |
| 323.15 | 1.2593      | 363.15 | 3.0980      |
| 333.15 | 1.6054      |        |             |

Table 3. Experimental speed of sound in the 70.1 wt.% R134a / 29.9 wt.% R227ea refrigerant in the vapor phase.

| $T$ (K) | $p$ (MPa) | $U$ (m s$^{-1}$) |
|--------|-----------|------------------|
| 323.15 | 1.2103    | 127.81           |
| 333.15 | 1.2797    | 132.25           |
| 353.15 | 1.4098    | 140.46           |
| 373.15 | 1.5350    | 147.71           |

Primary data on the density of superheated vapor were approximated by the eight-parameter Benedict – Webb – Rubin state equation [5]:

$$p = RTd + \left( a_1RT - a_2 - \frac{a_3}{T^2} \right) d^2 - (a_4RT - a_5)d^3 + a_6d^6 + \frac{a_7d^4}{T^2} \left( 1 + a_8d^2 \right) \exp \left( -a_9d^2 \right), \quad (1)$$
where \( p \) is the pressure in MPa, \( T \) is the temperature in K, \( d = (\rho M^{-1}) \) is the density in mol dm\(^3\), \( M = 116.375 \) (kg kmol\(^{-1}\)) is the molecular weight, \( R = 8.314472 \times 10^{-3} \) (MPa dm\(^3\) mol\(^{-1}\) K\(^{-1}\)) is universal gas constant. The coefficients of equation (1) are given in table. 4. The mean absolute deviation of experimental points from dependence (1) does not exceed 0.015\% (Fig. 2).

![Graph showing experimental quasi-isochores](image)

**Figure 1.** Experimental quasi-isochores of 69.2 wt.% R134a/30.8 wt.% R227ea refrigerant vapor density: 1 – 23.6 (kg m\(^{-3}\)), 2 – 35.7, 3 – 61.8, 4 – 101.0.

**Table 4.** Coefficients of the equation (1) for the 69.2 wt.% R134a / 30.8 wt.% R227ea refrigerant in the vapor phase.

| Coefficient | Value     |
|-------------|-----------|
| \( a_1 \) (dm\(^3\) mol\(^{-1}\)) | -0.10504  |
| \( a_2 \) (MPa dm\(^6\) mol\(^{-2}\)) | -0.2254   |
| \( a_3 \) (MPa K\(^2\) dm\(^6\) mol\(^{-2}\)) | 110943    |
| \( a_4 \) (dm\(^6\) mol\(^{-2}\)) | -0.10054  |
| \( a_5 \) (MPa dm\(^8\) mol\(^{-3}\)) | -0.29368  |
| \( a_6 \) (MPa dm\(^8\) mol\(^{-3}\)) | 0.05292   |
| \( a_7 \) (MPa K\(^2\) dm\(^8\) mol\(^{-3}\)) | 10565     |
| \( a_8 \) (dm\(^8\) mol\(^{-2}\)) | 0         |
The pressure on the dew line of the 69.2 wt.% R134a/30.8 wt.% R227ea refrigerant was determined by the position of the “kink” on the temperature dependence of pressure in the piezometer. Initial data were fitted by the Riedel equation:

\[
\ln p_d = 36.2983 - \frac{3769.06}{T} - 4.24225 \ln T + 9.539 \times 10^{-17} T^6,
\]

where \( p_d \) is in MPa, \( T \) is in Kelvin. The mean absolute deviation of the experimental points from (2) was 0.04%.

The speed of sound \( U \) of the 70.1 wt.% R134a / 29.9 wt.% R227ea refrigerant was measured along one quasi-isochore from 313 to 373 K and with an estimated error of 0.2–0.3%. The results of the experiments are given in Table 3

A comparison of the obtained data with the results of calculations using the REFPROP program (version 8.0) shows that the density values are, on average, 0.8% higher, and the vapor pressure on the dew line and the speed of sound are 1.3% and 0.4% lower than in [1]. This discrepancy exceeds the estimated errors of our measurements, so the results can be used to refine the program REFPROP.

**Conclusion**

For the first time, the pressure on the dew line, speed of sound and superheated vapor density were measured for two mixture refrigerants of the R134a-R227ea system in a wide range of state parameters. Approximation equations are obtained that allows one to calculate the properties of the investigated refrigerants at given temperature and pressure. It is shown that the calculations using the REFPROP program (version 8.0) deviate noticeably from the obtained experimental results.
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