

Viscosity of Refrigerants R12, R113, and R114 and Mixtures of R12 + R114 at High Pressure¹

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New viscosity measurements for the gaseous and supercritical state of the halogenated hydrocarbons R12, R113, and R114 and binary mixtures of R12 + R114 of different compositions are presented. The measurements were carried out at superheated and supercritical temperatures from 30 to 200°C and in the pressure range from 1 to 80 bar. Viscosity was measured with an oscillating-disk viscometer and the data obtained are relative to the viscosity of nitrogen. The estimated accuracy of the measured results is $\pm 0.6\%$. The results obtained show that, at subcritical temperatures, the pressure effect on viscosity is negative. This anomalous behaviour is investigated in detail in this work. At atmospheric pressure the viscosity of gas mixtures is almost a linear function of their composition. At high pressure, the residual viscosities $\eta - \eta_0$ of both the pure components and the mixtures were used to follow a single relationship versus the residual reduced density $\rho_{r,0}$.

KEY WORDS; gaseous mixtures; R12 + R114; refrigerants; R12; R113; R114; superheated and supercritical; viscosity.

1. INTRODUCTION

With respect to the new applications of halogenated hydrocarbons and their mixtures in various low-temperature power generating systems, investigations are necessary to define their viscosity in a wider range of pressure and temperature than used in refrigeration engineering. The existing experimental data of the viscosity of halogenated hydrocarbons cover mostly the compressed liquid state. For the gaseous state, the data are limited primarily to atmospheric pressure. Only a few measurements

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have been carried out at high pressure [1]. Experimental investigations on the viscosity of several binary mixtures of fluorocarbon refrigerants at atmospheric pressure have been reported recently [2]. To our knowledge, there is still a lack of information concerning the viscosity data of refrigerants at superheated and supercritical state. The purpose of this work is to present new measurements of the viscosity of the refrigerants R12, R113, and R114 and binary gaseous mixtures of R12+R114. The measurements were carried out at temperatures from 30 to 200°C and at pressures up to 80 bar.

2. EXPERIMENTAL PROCEDURE

The experiments were performed with the oscillating-disk viscometer shown in Fig. 1. The oscillating disk of $R=29.55$ -mm radius and

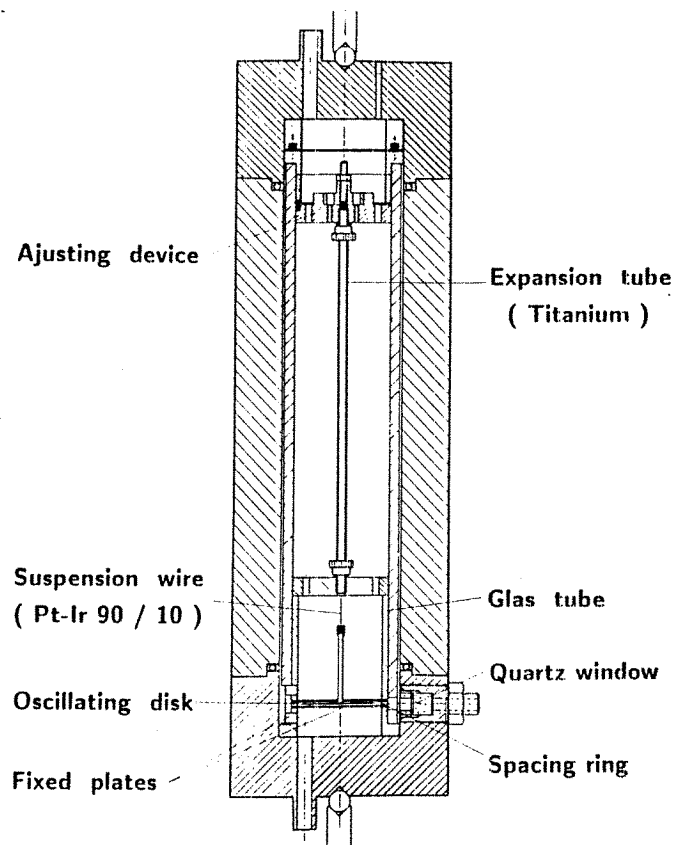


Fig. 1. Oscillating-disk viscometer.

$d=1.5$ -mm thickness was suspended by means of a platinum-iridium wire (90/10) of diameter $D=0.06$ mm. A spacer ring made of optically grounded quartz glass ensured the distance between the fixed plates. The clearances between oscillating disk and fixed plates were $b_1=b_2=1.01$ mm. The oscillating system was accommodated in a suspension holder by means of supports of different materials (titanium, glass), which compensated the thermal expansion of the wire to a great extent. The combination of the supports allowed an axial displacement of the disk of only 0.00045 mm/°C. The temperature of the fluid was established by five sectionwise controllable jacket-type heaters. The fluid temperature was measured with three thermocouples inside the viscometer positioned below and above the fixed plates. The temperature distribution within the viscometer was monitored with the aid of a series of thermocouples positioned on the wall of the viscometer. By this it was possible to impose a small and stable positive temperature gradient over the height of the viscometer in order to prevent the onset of natural convective flow in fluid.

The evaluation of the experiments was based on the relative method developed by Kestin et al. [3, 4]. To determine the viscosity by this method it was necessary to calibrate the viscometer with a well-known viscosity gas in order to obtain the edge effects (edge-correction factor) as a function of boundary layer thickness, defined as

$$\delta = (\eta T_0 / 2\pi\rho)^{1/2} \quad (1)$$

where η represents the dynamic viscosity and ρ the density. According to Kestin et al. [3], the following working formula for calibrating and evaluating of present measurements was used:

$$C = \frac{2(T_0/T)[\Delta(T_0/T) - \Delta_0]}{(\pi\rho R^4\delta/I)\{H_1K_2 + H_2K_1 + (2d/R)[H_1 + (3\delta T_0/2RT)]\}} \quad (2)$$

In Eq. (2), I is the moment of inertia of the suspension system, Δ and Δ_0 are the logarithmic decrements of damping, and T and T_0 are the periods of oscillation in media and in vacuum, respectively. Δ_0 and T_0 both depend on temperature and were obtained at temperatures ranging from 30 to 230°C in the viscometer itself. The remaining symbols have the following meaning:

$$H_{1,2} = \left(1 \mp \frac{3}{2}\Delta - \frac{3}{8}\Delta^2\right) \left[2\left(\frac{T}{T_0}\right)^3\right]^{-1/2} \quad (2a, b)$$

$$K_1 = \frac{\sin Y}{\cosh X - \cos Y}; \quad K_2 = \frac{\sinh X}{\cosh X - \cos Y} \quad (2c, d)$$

$$X, Y = \left(2 \frac{T}{T_0}\right)^{-1/2} \left(1 \mp \frac{1}{2} A + \frac{1}{8} A^2\right) \left(\frac{b_1 + b_2}{\delta}\right) \quad (2e, f)$$

$$A = \frac{1}{2\pi m} \ln \frac{\alpha_n}{\alpha_{n+m}} \quad (2g)$$

The edge-correction factor C was obtained by using nitrogen at temperatures ranging from 30 to 200°C and at pressures up to 80 bar. The values of C as a function of $1/\delta$ are shown in Fig. 2. It is assumed that a small upward displacement of the disk (~ 0.09 mm at 200°C) resulting from the differential thermal expansion should introduce any significant errors. In the range of large boundary layer thicknesses we have evaluated an instrument constant $C_N = 1.2193$. The related value determined by the calibration is $C_{(\delta=\infty)} = 1.2231$.

3. EXPERIMENTAL RESULTS

The viscosity of the refrigerants R12, R113, and R114 and three mixtures of R12 + R114 with compositions $x_{R12} = 25.7, 49.6,$ and 74.6% have been measured. x_{R12} represents the mass fraction of the R12 component. The measurements were carried out at superheated and supercritical temperatures ranging from 30 to 200°C and at pressures ranging from 1 to

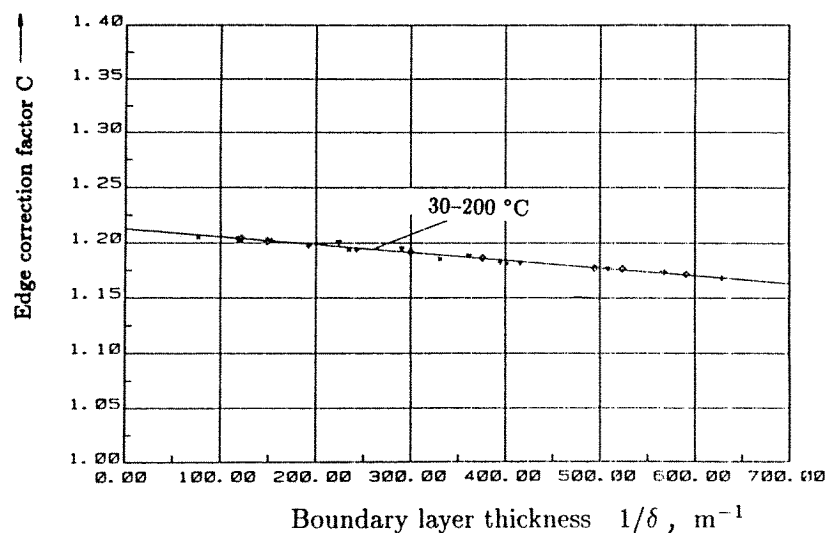


Fig. 2. Edge-correction factor C determined in nitrogen.

80 bar. The refrigerants had a purity of 99.8%. We estimate the absolute accuracy of our viscosity values to be 0.6% within the investigated range of temperature and pressure.

3.1. Viscosity at Low Pressure

The experimental results obtained for the viscosity of R12, R113, and R114 and the mixtures of R12 + R114 at atmospheric pressure are presented in Fig. 3. The results show that the viscosity of both the pure components and their mixtures can be represented within an average deviation of $\pm 0.4\%$ by a modified Sutherland equation. In addition, the results show that for all R12 + R114 mixtures, viscosity at atmospheric pressure are almost a linear function of concentration as

$$\eta_{0m} = x_1 \eta_1 + x_2 \eta_2 \quad (3)$$

where η_1 and η_2 are the viscosities, and x_1 and x_2 the mass fractions of the components.

For estimating the viscosity of gaseous mixtures at low pressure a number of correlations are reported in the literature [5-9]. By comparing our data with those methods we found that our data can be predicted

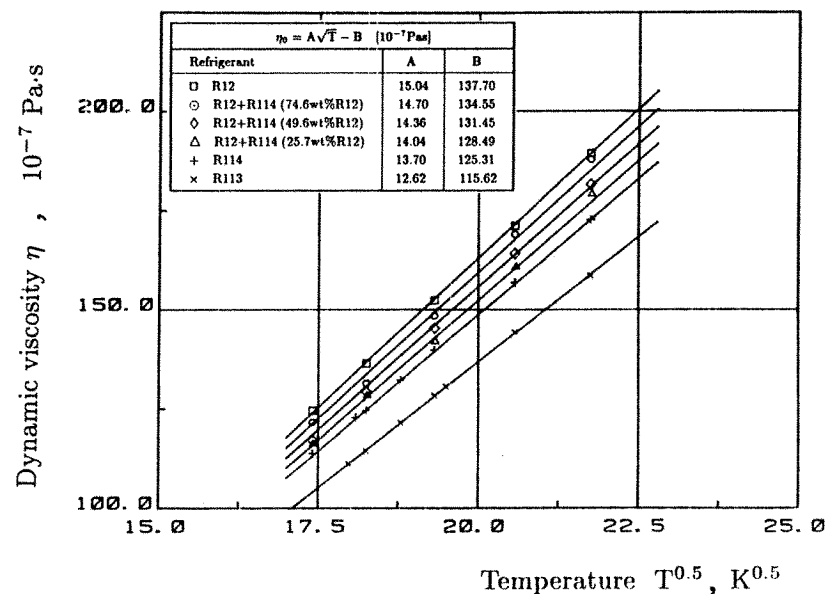


Fig. 3. Viscosity of R12, R113, R114, and R12 + R114 mixtures at atmospheric pressure.

successfully by the Sutherland relation type [7] and by the equation of Wilke [8]. The viscosity of binary gaseous mixtures at low pressure can be estimated by Sutherland relation as

$$\eta_{om} = \frac{\eta_1}{1 + \Phi_{12}(y_2/y_1)} + \frac{\eta_2}{1 + \Phi_{21}(y_1/y_2)} \quad (4)$$

where y_1 and y_2 are the mole fractions. Φ_{12} and Φ_{21} are the Sutherland coefficients and have the following interrelation:

$$\frac{\Phi_{12}}{\Phi_{21}} = \frac{\eta_1 M_2}{\eta_2 M_1} \quad (5)$$

M_1 and M_2 represent the molar mass of the components. By this procedure the values η_1 , η_2 , and η_{om} at one composition and at the same temperature must be known to establish the coefficients Φ_{12} and Φ_{21} . Based on our experimental results we obtained the optimum values of Sutherland coefficients for R12 + R114 mixtures as follows:

$$\Phi_{12} = 1.245, \quad \Phi_{21} = 0.808$$

A comparison between the experimental data and those computed by Eqs. (4) and (5) are represented in Fig. 4. We see that the results can be

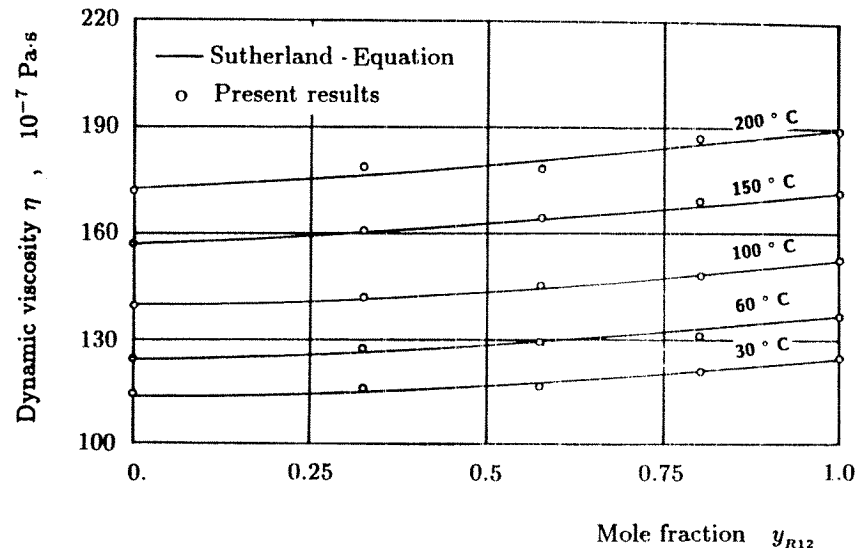


Fig. 4. Comparison of viscosity of R12 + R114 mixtures at low pressure with the Sutherland equation (4).

reproduced with an average absolute deviation of 0.7% over the entire temperature range from 30 to 200°C. We also found that, within the temperature range investigated, the Sutherland coefficients Φ_{12} and Φ_{21} can be treated as temperature independent.

For binary gaseous mixtures the equation of Wilke is identical to Eq. (4). Bromley and Wilke [8] have suggested the following relation to represent the coefficient Φ_{12} :

$$\Phi_{12} = \frac{[1 + (\eta_1/\eta_2)^{1/2} (M_2/M_1)^{1/4}]^2}{2\sqrt{2} [1 + M_1/M_2]^{1/2}} \quad (6)$$

where for interrelation of Φ_{12} and Φ_{21} , Eq. (5) can be used. According to Eq. (6), we have computed the following values for coefficients Φ_{12} and Φ_{21} :

$$\Phi_{12} = 1.237, \quad \Phi_{21} = 0.803$$

which agree with a deviation of 0.6% with those computed from experimental mixture viscosity η_{om} by using Eqs. (4) and (5). A comparison between our results and those calculated by the equation of Wilke shows a mean deviation up to 1%.

3.2. Viscosity at High Pressure

At highly superheated and supercritical temperatures the viscosity increases with increasing pressure (density), whereas at subcritical temperatures the viscosity of halogenated hydrocarbons R12, R113, and R114 and the mixtures of R12 + R114 reveals an anomalous behavior in which the viscosity decreases with increasing pressure. A negative pressure effect on the viscosity of steam at subcritical temperatures was observed first by Kestin and Wang [10]. It seems that the viscosity of halogenated hydrocarbons also follows the same behavior. An extensive experimental investigation was performed to obtain the temperature at which a negative pressure effect inverts into a positive one. The results presented in Fig. 5 show the effect of pressure on the viscosity of R113. From the information illustrated in Fig. 5, we can see that the isotherm 107°C could be adapted as an "inversion line" for R113, along which the viscosity values of R113 remain constant with increasing pressure. The inversion line for R114 was measured at a temperature of about 54°C. Although the absolute values of these inversion temperatures are different for both refrigerants, with respect to their critical temperatures T_c , they predict an almost equally reduced temperature T_r as

$$T_r = T/T_c = 0.78 \quad (7)$$

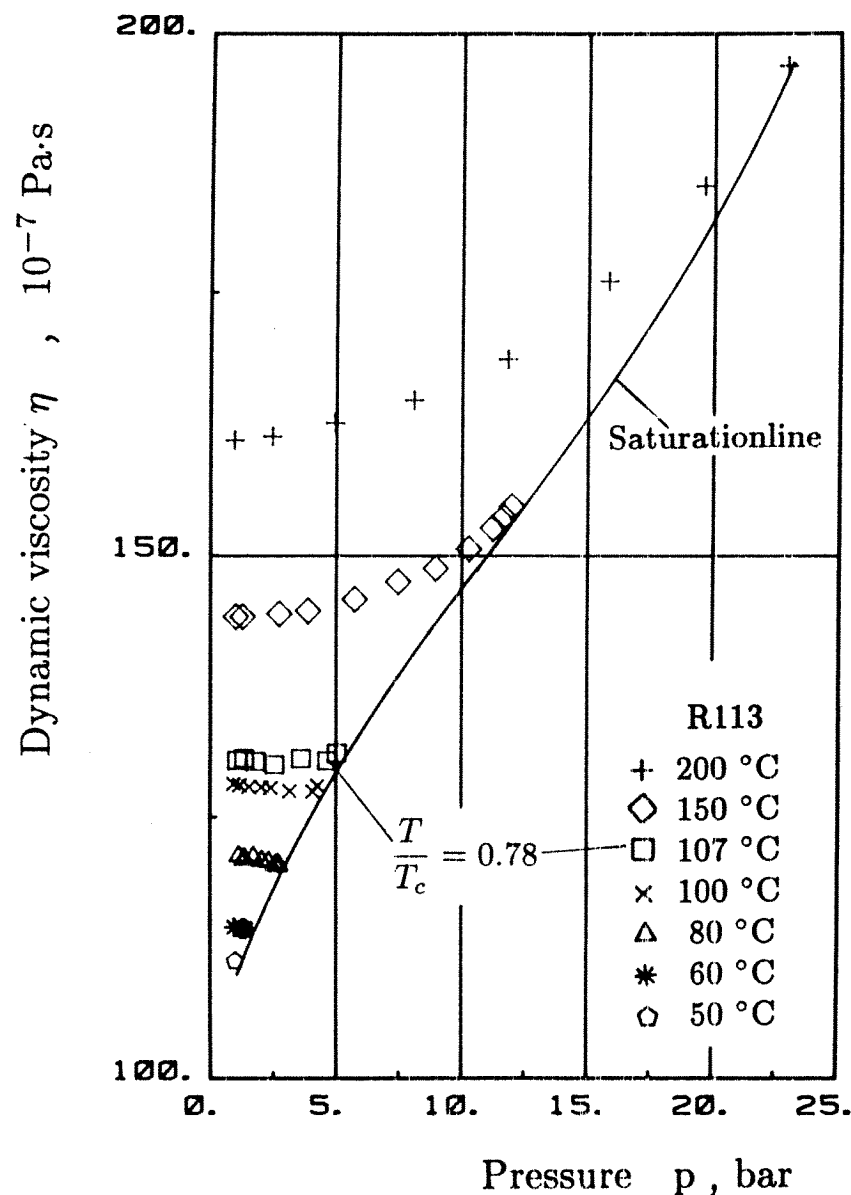


Fig. 5. Viscosity of R113 in terms of pressure and temperature.

Using this simple relation we obtain an inversion temperature of about 27°C for R12. As a result, for investigated refrigerants the pressure effect on the viscosity is positive above $T_r=0.78$, while the pressure effect on the viscosity is negative below that.

Above the reduced temperature $T_r=0.78$, the viscosity values along the isotherms form parallel curves as a function of density. The similar behavior of the viscosity of both the pure components and the mixtures investigated illustrates that using the residual viscosity ($\eta - \eta_0$) method could be an appropriate technique for predicting the viscosity of these substances at high pressure. To apply this procedure, reliable density data or an applicable equation of state is required to determine the viscosity in a reasonable extent. Concerning the mixtures, the dependency of density upon composition must be also known. As a first step, we have used the corresponding-states law [11, 12] to calculate the densities of R12, R113, R114, and R12 + R114 mixtures. In order to prove the reliability of densities calculated by this method we compared them with the experimental data, which were available in the literature [13–15]. The comparisons have shown standard deviations up to 1.2% for R12, 1% for R113, and 1.4% for R114, respectively. To use the corresponding-states law for mixtures of R12 + R114, the pseudocritical pressure P_{cm} and the pseudocritical temperature T_{cm} must be established. To obtain these properties, the procedure suggested by Prausnitz and Gunn [16] was used. The molar mass and the acentric factor of the mixture were evaluated by the mole fraction average method.

Using our experimental values of the viscosity at atmospheric pressure η_0 , we computed the residual viscosity of all substances. In addition, it was appropriate for our proposal to determine a “reduced residual density” by

$$\rho_{r0} = \frac{\rho - \rho_0}{\rho_c} \quad (8)$$

to eliminate the small differences of the densities ρ_0 of the different refrigerants at atmospheric pressure. The evaluated values of residual viscosity ($\eta - \eta_0$) as a function of reduced residual density ρ_{r0} are presented in Fig. 6. So we can see that the residual viscosity values of R12, R113, R114, and R12 + R114 mixtures follow a single relationship at the temperatures above the reduced temperature of $T_r=0.78$. Below this the correspondence of the data is no longer satisfactory, although the differences between the absolute values of the viscosity is very small. In this range we have to consider not only the influence of density but also the influence of temperature on the residual viscosity, which is not incorporated in the atmospheric viscosity η_0 .

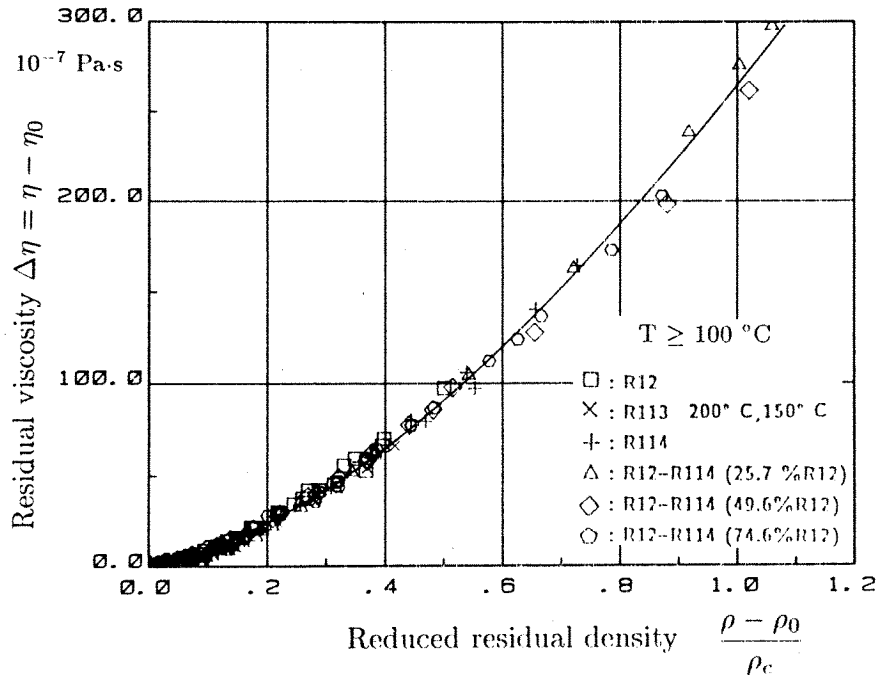


Fig. 6. Residual viscosity of R12, R113, R114, and R12 + R114 mixtures in terms of reduced residual density.

Based on the principles of the corresponding-states and the residual viscosity method [6, 17] and considering the investigated substances as nonpolar gases, we present the following equation for predicting the viscosity of halogenated hydrocarbons R12, R113, and R114 and the mixtures of R12 + R114, which includes also the influence of the temperature in the region of negative pressure effect on the viscosity.

$$[\eta - \eta_0] \xi z_c = T_r^{-2.2} [\ln(1.65 + \rho_{r0}^{0.8})]^{1.6} [e^{(1 - 0.78/T_r) \cdot \rho_0} - 1] \quad (9)$$

The factor ξ suggested by Lucas [6] and the critical compressibility factor z_c are defined as

$$\xi = \frac{T_c^{1/6} R^{1/6} N_0^{1/3}}{M^{1/2} p_c^{2/3}} \quad \text{and} \quad z_c = \frac{P_c V_c}{RT_c} \quad (10a, b)$$

In Eqs. (10a) and (10b), the units used are $R = 8314$ in $\text{kJ} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$, N_0 (Avogadro's number) $= 6.023 \times 10^{26}$ in kmol^{-1} , T_c in K, P_c in $\text{N} \cdot \text{m}^{-2}$, M in $\text{kg} \cdot \text{kmol}^{-1}$, V_c in $\text{m}^3 \cdot \text{kmol}^{-1}$, and ξ in $(\text{Pa} \cdot \text{s})^{-1}$.

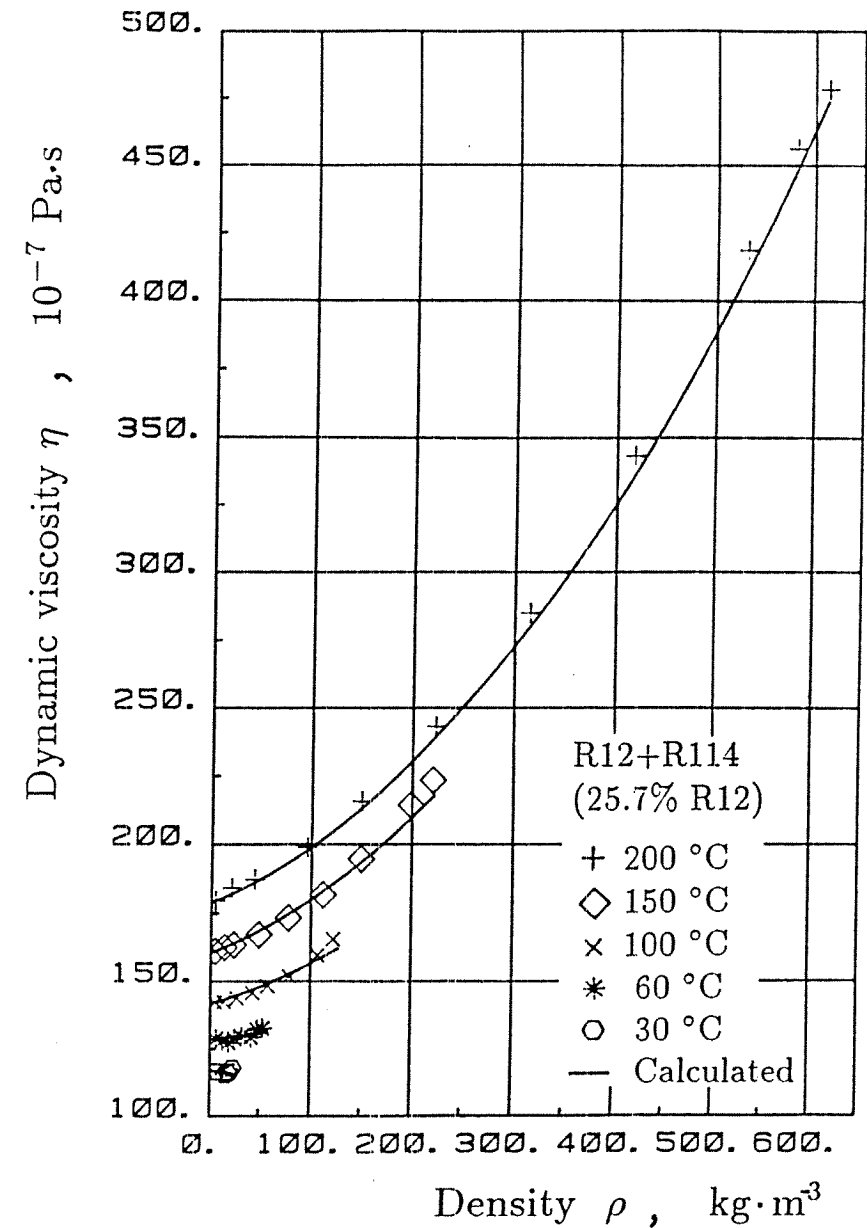


Fig. 7. Comparison of the experimental viscosity of an R12 + R114 mixture (25.7 wt% R12) with Eq. (9).

A representative comparison between the experimental values of the viscosity η as a function of density ρ for the R12 + R114 mixture ($x_{R12} = 25.7\%$) and those correlated by Eq. (9) is shown in Fig. 7. We note here that Eq. (9) can present the viscosity values of refrigerants R12, R113, and R114 and the mixtures of R12 + R114 at high pressure with a deviation of $\pm 1.2\%$. Only a few measurement points of R12 at the isotherms 100 and 150°C somewhat exceed this accuracy range.

4. CONCLUSIONS

The experimental results show a similar behavior of the viscosity of halogenated hydrocarbons, R12, R113, and R114 and gaseous mixtures of R12 + R114. At temperatures below the reduced temperature of $T_r = 0.78$, the viscosity decreases with increasing pressure, while at temperatures above this the viscosity increases with pressure. At atmospheric pressure the viscosity of R12 + R114 mixtures changes almost linearly with composition. It can be presented by Sutherland's relation or the equation of Wilke with a mean deviation up to 1%. The viscosity of all substance at high pressure can be correlated by a single equation based on the principle of residual viscosity method. A new correlation which represent our data with an accuracy of $\pm 1.2\%$ is introduced.

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