

VISCOSITY OF GASEOUS R123, R134a AND R142b

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Abstract

The viscosity of the environmentally acceptable working fluids R123, R134a and R142b has been measured at temperatures from 30 to 150°C and at pressures from 0.1 to 6.5 MPa. The measurements were carried out in an oscillating - disk viscometer and the data obtained are relative to the viscosity of nitrogen. The accuracy of the reported viscosities is estimated to be $\pm 0.5\%$.

At atmospheric pressure, the viscosity of the investigated substances can be represented by the Chapman - Enskog equation with a mean deviation of $\pm 0.3\%$. At high pressure, the viscosity of each of the fluids reveals an anomalous behaviour at subcritical temperatures in which the pressure effect on the viscosity is negative. This negative pressure effect inverts to a positive one at the reduced temperature of about $T_r = 0.78$. Above this temperature, the residual viscosities of R123, R134a and R142b obey the law of corresponding states and can be represented with the same empirical equation which was previously developed for several other refrigerants.

1. Introduction

Due to the negative impact of fully halogenated hydrocarbons (CFCs) on the environment, it became necessary to replace these substances with a set of environmentally acceptable hydrogen containing hydrocarbons (HCFCs) and their mixtures which have been identified to be the most promising alternatives. R134a (CH_2FCF_3) has been developed to replace the refrigerant R12 and R123 (CCl_2HCF_3) is proposed to be an alternative for the refrigerant R11. The refrigerant R142b, known since many years,

is indeed a flammable fluid, but mixtures of R142b and the most available and also environmentally acceptable refrigerant R22, at concentrations above 40 % R22, yield nonflammable products which might also be considered as possible alternatives.

Thermophysical property data in general, and the transport properties of these fluids in particular, are needed for the new design of efficient refrigeration equipments, or the modification of existing systems, which use them as working fluids. In addition, the new substances will possibly be used as working fluids in various intermediate temperature power generating systems. It is therefore necessary to define their thermophysical properties in a wider range of temperature and pressure than that used in refrigeration engineering.

In a series of measurements we have investigated the influence of temperature and pressure on the viscosity of several pure refrigerants and their mixtures. The results of the measurements for R12, R113, R114 and mixtures of R12+R114 were reported in an earlier work (Nabizadeh and Mayinger 1989a). The new viscosity values for R22 and mixtures of R22+R114 have been presented recently (Nabizadeh and Mayinger 1989b,1990). In continuation to our earlier investigations, we present in this paper the new viscosity measurements for R123, R134a and R142b in the gas phase. The experimental results indicate that the viscosity of each of the already investigated refrigerants is characterised by an " inversion temperature ", which could experimentally be defined at a reduced temperature of about $T_r = 0.78$. Above this temperature the pressure effect on the viscosities of these fluids is positive and follows the simple gas rules, while it is negative below this temperature. In addition, it was found out that the viscosities of these systems reveal a similar behaviour at moderate densities and obey the law of corresponding states. A single relationship between the residual viscosity, reduced temperature and the reduced density can be used to predict these viscosities at high pressure. The new measurements should also help to verify if these alternative refrigerants behave similarly and obey the law of corresponding states.

2. Experimental Procedure

The measurements were carried out in the same oscillating - disk viscometer, which has been used for our earlier viscosity measurements. The basic principle of design and calibration of the viscometer were described in detail in an earlier work (Nabizadeh

and Mayinger 1989a). The characteristics of the suspension system employed for the present measurements are the same as given in reference (Nabizadeh and Mayinger 1990). The experiments were performed at pressures ranging from 0.1 to 6.5 MPa and in the temperature ranges 30 - 150°C for R123 and R134a, and 30 - 100°C for R142b. The upper temperature limits were set in order to avoid thermal decomposition of the fluids. The evaluation of the experiments was based on the relative method developed by Kestin et al. (Kestin, Leidenfrost and Liu 1959, Kestin and Whitelaw 1963). Prior to the new viscosity measurements the viscometer was calibrated with nitrogen in order to determine the edge - correction factor C, required for the evaluation of the data. The viscosity values of nitrogen were taken from the reference (Stephan, Krauss and Laesecke 1987).

With respect to our earlier observation, the instrument was particularly calibrated at the temperatures at which the viscosity was to be measured, in order to consider also the influence of small upward shifting of the oscillating - disk relative to the fixed plates. Fig. 1 represents the values of edge - correction factor C obtained with nitrogen

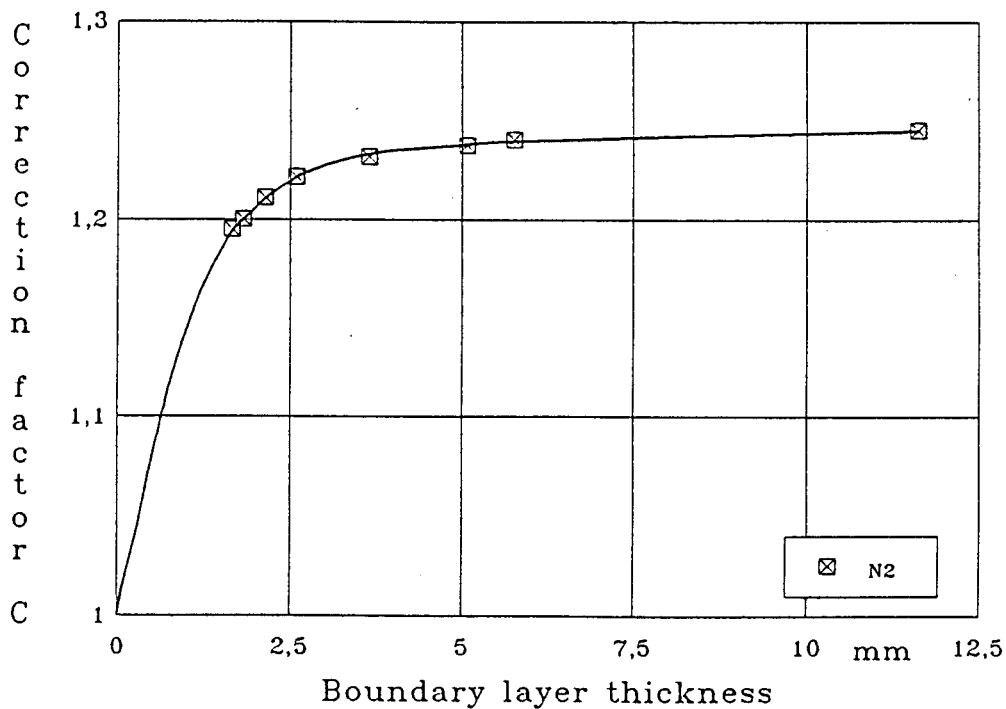


Fig. 1. Calibration curve at 100°C

at the temperature 100°C , as a function of boundary layer thickness δ , defined as:

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

where η is the viscosity and ρ the density of the fluid. T_0 is the period of oscillation in vacuum. The deviation between the fitted values and the calibration curve did not exceed $\pm 0.15\%$.

The fluids were all supplied by Kali - Chemie AG. Hannover, FRG. The densities of the fluids were evaluated, with the aid of the given correlations in the references (Kabelac and Baehr 1989, Weber 1989a) for R134a, (Weber 1989b, Döring and Buchwald 1989) for R123 and (Döring 1989) for R142b.

3. Experimental Results

The results of the experiment on the fluids R123, R134a and R142b in the gas phase are given in Tables 1, 2 and 3 respectively. These tables also contain the densities which have been used for the evaluation of present measurements. Based on these density values, the uncertainty of the reported data is estimated to be $\pm 0.5\%$. Figs. 2 to 4 show the viscosities of R123, R142b and R134a in terms of pressure and nominal temperatures respectively. For which the primary value of the viscosities were corrected for the nominal temperatures by means of small linear corrections which, in any case, did not exceed 0.15%. Due to the upper limits of the temperature for each substance, only the viscosity measurements of R134a could be extended to the supercritical region, while those of R123 and R142b were limited to the subcritical temperatures.

At the subcritical isotherms 60°C for R123 and 30°C for R142b, as shown in Figs. 2 and 3 respectively, the viscosities of these fluids decrease with increasing pressure. Such a negative pressure effect was observed earlier (Nabizadeh and Mayinger 1989b) on the viscosities of other refrigerants too . Additional measurements were therefore necessary to obtain the isotherms, along which the viscosity of those substances are independent of pressure and a negative pressure effect inverts to a positive one. Fig. 5 shows the inversion isotherms of the alternative refrigerants R123 and R142b together with the experimental results of the refrigerants R113 and R114.

TABLE 1. Viscosity of gaseous R123 (CCl_2HCF_3)

T [°C]	p [MPa]	ρ [kg/m ³]	η [μ Pa s]
29.93	0.1106	7.048	11.001
29.92	0.1016	6.448	11.013
29.95	0.1010	6.497	10.979
39.86	0.1574	9.844	11.324
39.86	0.1358	8.417	11.318
39.96	0.1101	6.750	11.329
59.20	0.2726	16.487	11.960
59.52	0.2222	13.188	12.028
59.58	0.1448	8.373	12.039
59.75	0.1010	5.755	12.076
84.26	0.5264	31.135	12.850
84.14	0.5120	30.166	12.820
83.84	0.4436	25.640	12.824
84.25	0.3554	19.999	12.822
84.01	0.2348	12.802	12.835
83.88	0.1150	6.086	12.845
99.78	0.7640	45.226	13.557
99.40	0.7388	43.493	13.547
99.48	0.6380	36.499	13.488
99.39	0.4382	23.814	13.422
99.28	0.2852	14.955	13.415
99.31	0.1100	5.552	13.399
149.72	2.0276	133.738	17.785
149.78	1.9142	120.766	17.332
149.85	1.7576	105.163	16.847
149.70	1.4858	83.257	16.171
149.92	1.1582	60.442	15.702
149.67	0.8306	40.638	15.354
149.56	0.5408	25.352	15.210
150.09	0.3608	16.442	15.141
150.26	0.1016	4.469	15.060

TABLE 2. Viscosity of gaseous R134a (CH_2FCF_3)

T [°C]	p [MPa]	ρ [kg/m ³]	η [μ Pa s]
30.01	0.746	36.105	12.141
29.91	0.740	35.790	12.123
29.84	0.706	33.810	12.119
29.93	0.636	29.820	12.114
29.92	0.552	25.265	12.117
29.93	0.438	19.500	12.117
29.72	0.316	13.665	12.117
29.81	0.100	4.130	12.095
60.29	1.653	84.778	14.340
60.21	1.597	80.483	14.263
60.13	1.270	58.525	13.792
60.07	1.018	44.355	13.654
60.07	0.751	31.085	13.506
59.99	0.517	20.565	13.456
60.05	0.216	8.185	13.402
60.16	0.102	3.805	13.408
95.64	3.412	213.669	20.815
95.51	3.334	201.183	20.537
95.60	3.178	179.120	19.431
95.72	2.917	150.645	18.272
95.78	2.517	117.730	17.163
95.70	2.006	85.249	16.145
95.65	1.511	59.585	15.551
95.60	1.025	37.985	15.106
95.71	0.651	23.100	14.850
95.57	0.330	11.345	14.694
95.74	0.101	3.360	14.663
151.18	6.425	323.873	28.913
150.76	6.349	318.758	28.575
150.47	6.023	291.392	27.107
150.50	5.780	263.327	25.597
150.15	5.007	215.330	23.329
150.01	4.474	181.892	21.809
150.18	4.002	155.123	20.692
150.69	3.424	125.599	19.767
150.63	2.991	105.814	18.927
150.55	2.494	84.904	18.328
150.63	1.752	56.540	17.595
150.51	1.012	31.135	17.106
150.97	0.541	16.140	16.876
151.30	0.100	2.910	16.693

TABLE 3. Viscosity of gaseous R142b ($CClF_2CH_3$)

T [°C]	p [MPa]	ρ [kg/m ³]	η [μ Pa s]
30.43	0.393	17.369	10.671
30.39	0.359	15.705	10.665
30.49	0.325	14.064	10.519
30.52	0.213	8.953	10.749
30.59	0.101	4.119	10.758
46.87	0.615	26.719	11.349
46.79	0.602	26.095	11.353
46.78	0.492	20.742	11.350
46.75	0.404	16.663	11.313
46.72	0.327	13.229	11.330
46.76	0.228	9.015	11.350
46.77	0.100	3.855	11.356
60.01	0.856	37.111	11.931
59.86	0.836	36.099	11.924
60.01	0.723	30.326	11.872
59.90	0.570	23.090	11.857
59.95	0.490	19.536	11.845
59.93	0.318	12.213	11.841
59.82	0.100	3.694	11.810
99.45	1.988	94.082	14.885
99.25	1.849	83.791	14.508
99.17	1.624	69.119	14.127
99.09	1.426	57.852	13.852
99.10	1.183	45.540	13.579
99.13	0.989	36.672	13.459
99.32	0.753	26.765	13.358
99.13	0.561	19.347	13.214
99.29	0.355	11.863	13.165
99.59	0.101	3.314	13.090

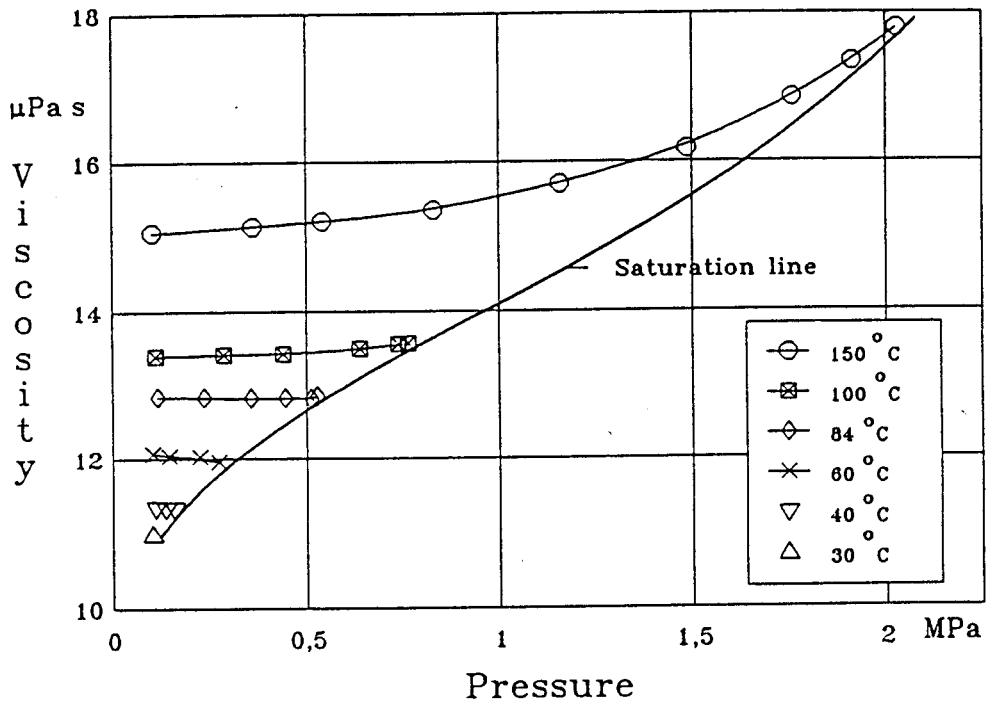


Fig. 2. Viscosity of alternative refrigerant R123 in terms of pressure

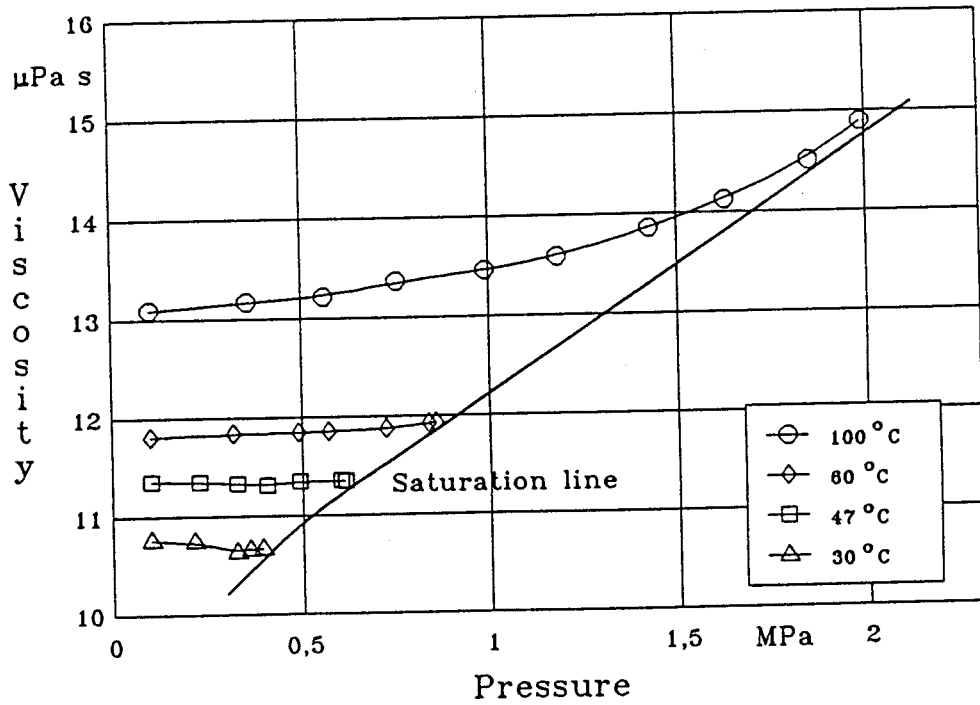


Fig. 3. Viscosity of alternative refrigerant R142b in terms of pressure

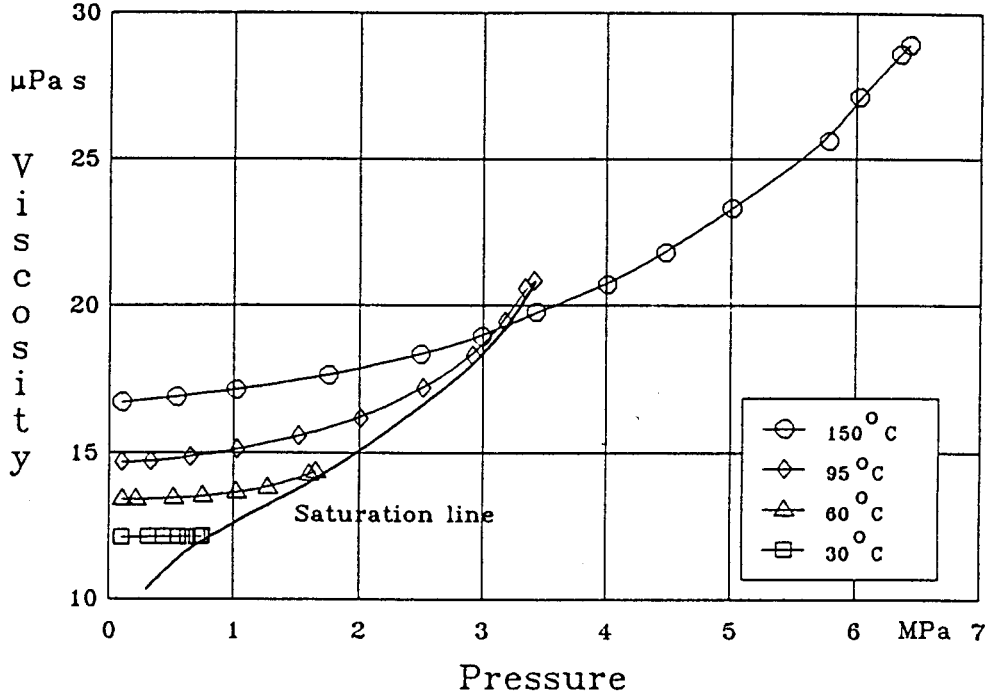


Fig. 4. Viscosity of alternative refrigerant R134a in terms of pressure

In this figure, the absolute values of the inversion temperatures of each fluid are also given. Although these temperatures are different for each substance, they can be normalised at the reduced temperature T_r of about

$$T_r = \frac{T_{inv}}{T_c} = 0.78 \quad (2)$$

for all the substances, where T_c represents the critical temperature. This therefore confirms the validity of our estimation obtained from the previous experiments. From the trend of the isotherms for R134a, shown in Fig. 4, we expect the same behaviour for this fluid too. According to relation (2), we estimate an inversion temperature of about 18°C for R134a which lies out of our temperature range and could not be defined by measurements. From the results of the earlier and present experiments on several refrigerants and their mixtures, we deduce that the viscosities of the alternative refrigerants at subcritical temperatures are also characterised by an inversion temperature which is defined at the same reduced temperature as given in relation (2).

In a graph of viscosity against pressure, as shown in Fig. 4 for R134a, the isotherms 95°C and 150°C (supercritical) intercept. This interception is due to the dependency

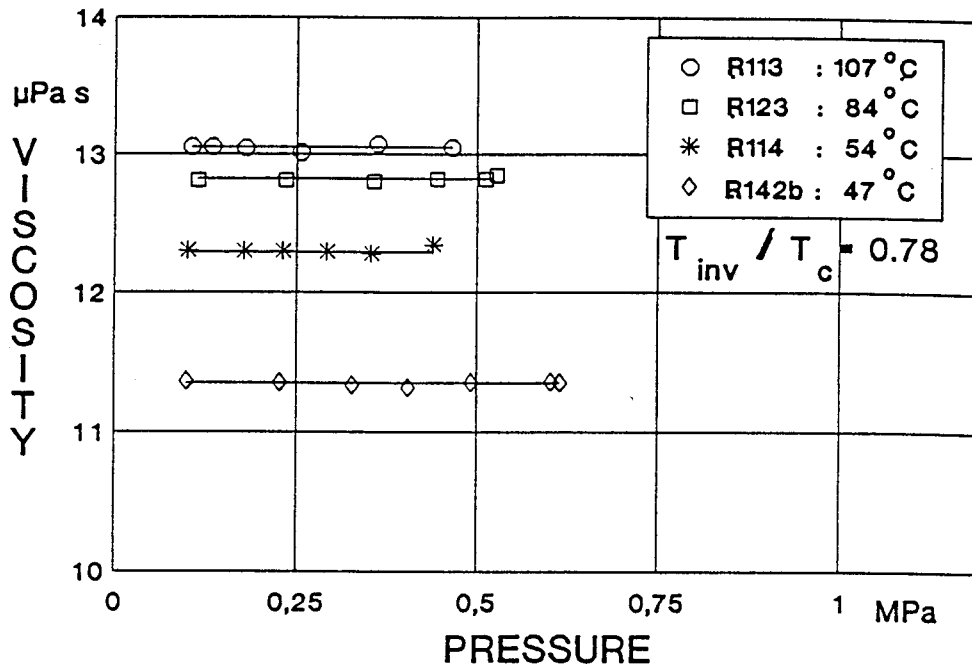


Fig. 5. Inversion isotherms of refrigerants R113, R114, R142b and alternative substance R123

of density on pressure and is eliminated if the viscosity is plotted against density, as illustrated in Fig. 6. In this case the isotherms, above the inversion temperature, run almost parallel to each other. This holds for all already investigated refrigerants.

Such a behaviour of these substances indicates that the residual viscosity method, $\eta - \eta_0$, would be appropriate to correlate the measured viscosity, of each of them as a function of its density. In this region, temperature effects are almost incorporated in the low pressure viscosity η_0 . The situation is different for the isotherms below the inversion temperature $T_r < 0.78$, where the pressure effect on the viscosity is negative and the temperature effect on the viscosity is more pronounced. In order to also use the residual viscosity method in this region, additional temperature effect, which is not incorporated in the η_0 term, should be considered besides the density. For this procedure, accurate viscosity data for low pressure viscosity η_0 , in this case at atmospheric pressure, are needed. Special effort therefore has to be made in order to obtain very accurate values of η_0 . For this reason, our experimental results are evaluated at low and at high pressures separately.

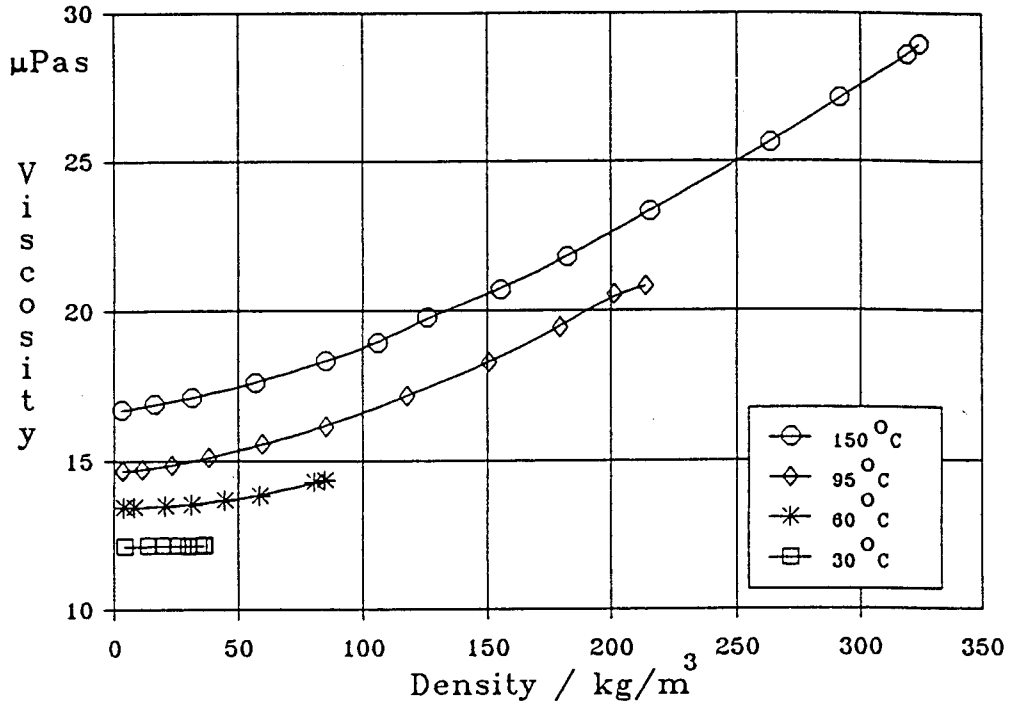


Fig. 6. Viscosity of R134a in terms of density

3.1. Viscosity of R123, R134a and R142b at low pressure

According to the rigorous kinetic theory of gases, the viscosity of a dilute gas is given by the Chapman - Enskog equation

$$\eta_0 = \frac{5}{16} \cdot \left(\frac{kMT}{\pi N_0} \right)^{1/2} \cdot \frac{1}{\sigma^2 \cdot \Omega_\eta(T^*)} \quad (3)$$

where k is the Boltzmann's constant, and N_0 the Avogadro's number. To use this relation, the collision diameter σ and the collision integral Ω_η must be known. The collision integral Ω_η is a function of the reduced temperature T^* defined as:

$$T^* = \frac{kT}{\epsilon} \quad (4)$$

The parameter ϵ is the potential energy of interaction between the molecules. The two parameters ϵ and σ can be conversely determined from the experimental viscosity of dilute gases (Hirschfelder, Curtiss and Bird 1966), where the adjusted parameters, treated as scaling factors, are only valid for the selected values of Ω_η . In a series of systematic investigations, accompanied by precise viscosity measurements, Kestin

and co-workers (Kestin, Ro and Wakeham 1972) developed the following empirical expression for the collision integral Ω_η :

$$\Omega_\eta = \exp[0.45667 - 0.53955(\ln T^*) + 0.187265(\ln T^*)^2 - 0.03629(\ln T^*)^3 + 0.00241(\ln T^*)^4] \quad (5)$$

Kestin and Wakeham (1979) have further proved, successfully, the validity of equation (5) for some polar gases, including refrigerant R22 with the reduced dipole moment of $\delta^* = 0.247$. Based on equation (5), we were able to represent our experimental data for R22, R114 and binary mixtures of these substances (Nabizadeh and Mayinger 1990) with a mean deviation of $\pm 0.3\%$. In present work, we also used equations (3) to (5) to correlate the experimental viscosity of the pure refrigerants R123, R134a and R142b. The optimum values of the parameters ϵ or ϵ/k and σ , evaluated from the best fit to our measured data are listed in Table 4.

Table 4. Scaling Parameters for R123, R134a and R142b

Substance	ϵ/k [K]	σ [nm]
R123	275.16	0.5909
R134a	277.74	0.5067
R142b	278.20	0.5362

Fig. 7 represents the deviations of the experimental data from the calculated values, using equations (3) to (5) and the scaling parameters from Table 4. The maximum deviation of all measurements from the correlation amounts to $\pm 0.5\%$, while the mean deviation is $\pm 0.25\%$. We may therefore conclude that equations (3) to (5) provide an equally good representation of the present data for the alternative refrigerants R123, R134a and R142b.

In addition, we note here that R123 should replace the refrigerant R11, and R134a is developed as an alternative for the refrigerant R12. A comparison of the viscosities of these substances, at low pressure, is displayed in Fig. 8 in terms of temperature. As can be seen, the viscosity of R134a is almost 3.7% smaller than that of R12, while the viscosities of R123 and R11 have the same value.

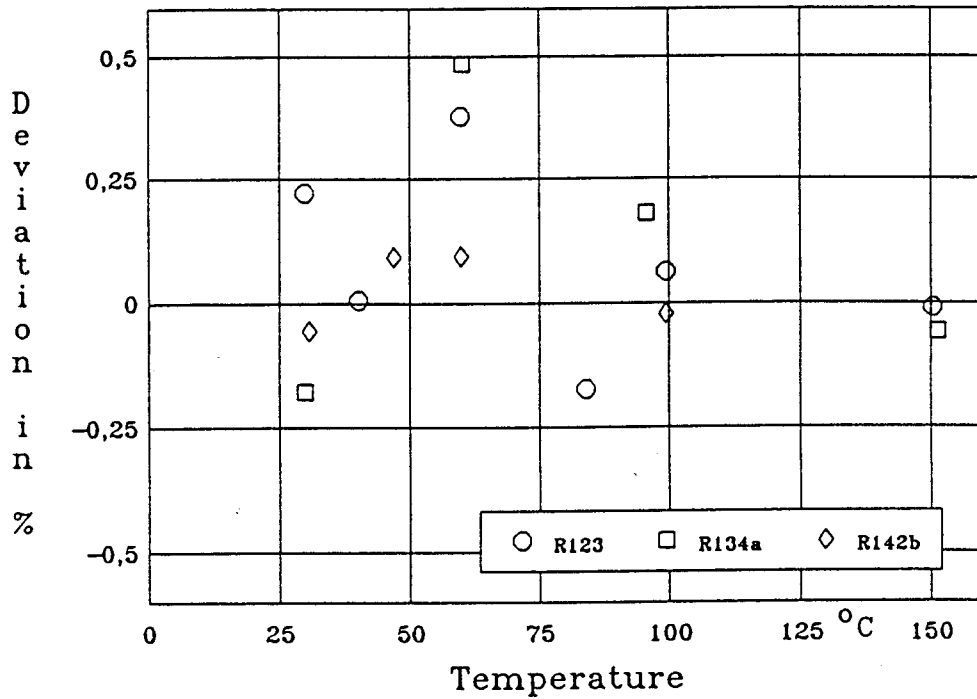


Fig. 7. Deviations of measured viscosity of R123, R134a and R142b from the calculated values by equation (3) at atmospheric pressure

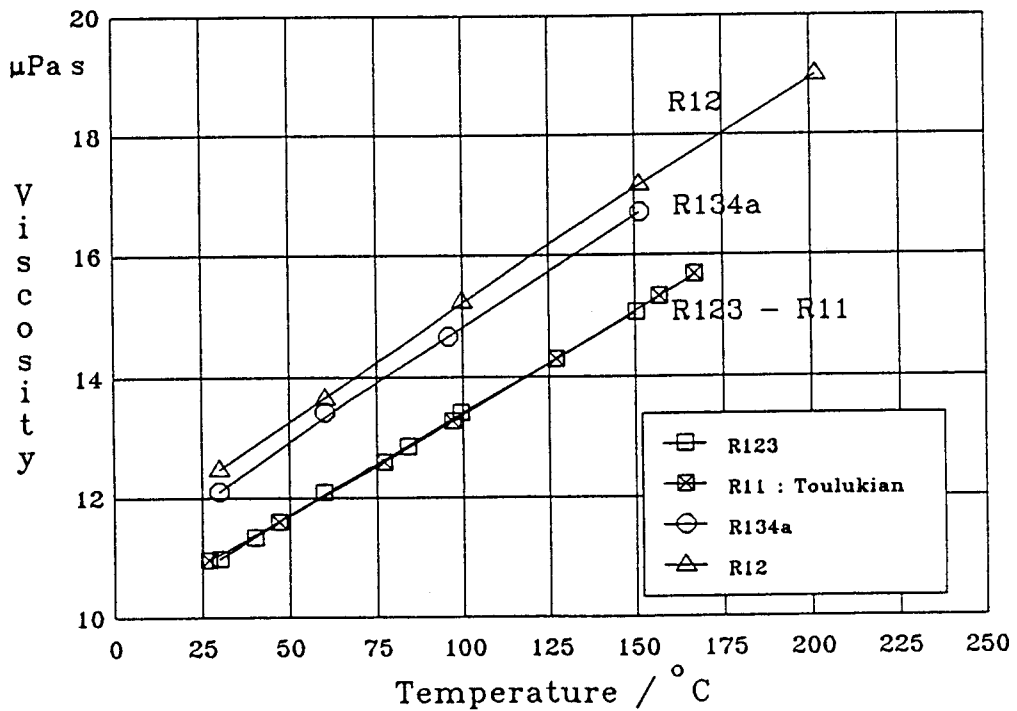


Fig. 8. Comparison between the viscosities of R11 and R12 with their alternatives R123 and R134a at atmospheric pressure

3.2. Viscosity of R123, R134a and R142b at high pressure.

Using the experimental values of the zero-viscosity η_0 , obtained in the present work at atmospheric pressure, we calculated the residual viscosity, $\Delta\eta = \eta - \eta_0$, of each substance at temperatures above the inversion temperature $T_r = 0.78$. The results are presented in Fig. 9 in terms of a normalised density, defined as:

$$\rho_{r_0} = \frac{\rho - \rho_0}{\rho_c} \quad (6)$$

where ρ_0 represents the density at atmospheric pressure and ρ_c the critical density.

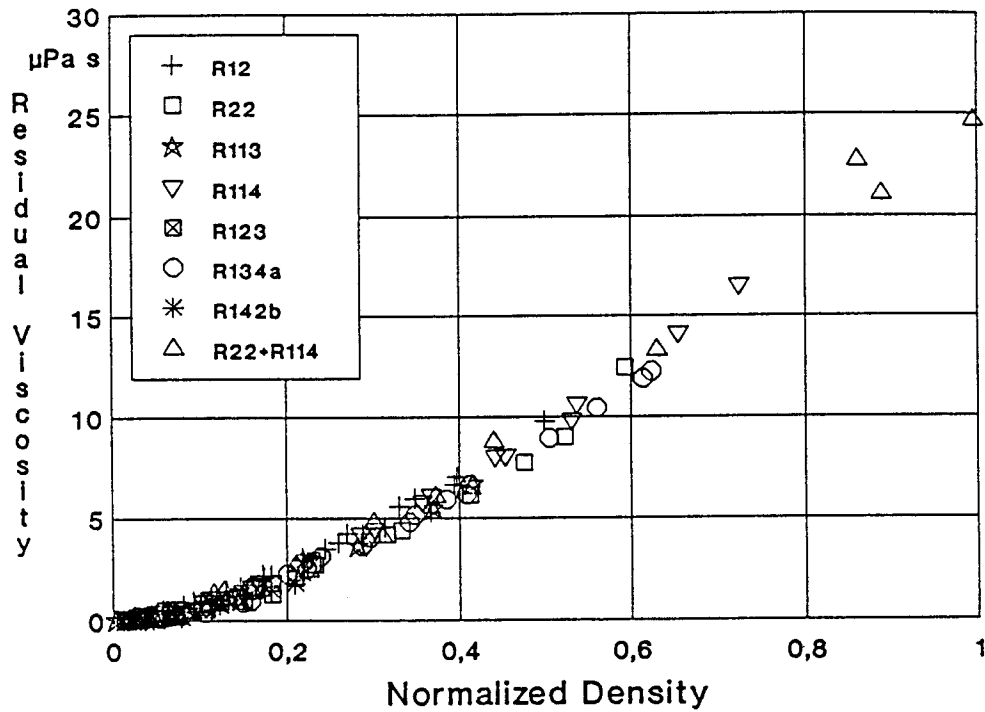


Fig. 9. Residual viscosity of refrigerants and their mixtures

This definition for ρ_{r_0} was appropriate to be used for this proposal, in order to eliminate the small differences of the densities ρ_0 of the different refrigerants at atmospheric pressure. For comparison, Fig. 9 also contains the experimental values of the residual viscosities for several other refrigerants and their mixtures from our earlier works (Nabizadeh and Mayinger 1989,1990). It is worth mentioning that these values were all obtained in the same apparatus under the same experimental conditions. As illustrated in Fig. 9, it is obvious that the residual viscosities of the new substances correspond to

those of the other refrigerants at moderate densities. A similar behaviour of the residual viscosities of different refrigerants indicates that a single relationship can be used for predicting the viscosities of these substances at high pressure. The only difference will then be in the determination of their zero - viscosities at low pressure. In our previous works (Nabizadeh and Mayinger 1989,1990), we have presented an empirical equation for correlating the residual viscosities of refrigerants and their mixtures, which was developed from our previous experiments and also incorporates the influence of temperature on the absolute viscosity in the region of the negative pressure effect. The correlation was based on the following principles:

- (i) The gaseous viscosity of the refrigerants obey the principle of corresponding states.
- (ii) The dependency of pressure (density) on the viscosity is characterised by an inversion temperature, which is defined at the same reduced temperature $T_r = 0.78$ for all investigated refrigerants.

During the course of present work, the new experimental values of residual viscosities of the alternative refrigerants R123, R134a and R142b could be represented by the same equation, which is defined as follows:

$$[\Delta\eta] \xi z_c = T_r^{-2.2} [\ln (1.65 + \rho_{r0}^{0.8})]^{1.6} \left[e^{(1-0.78/T_r) \cdot \rho_{r0}} - 1 \right] \quad (7)$$

The factor ξ , deduced from the law of corresponding states and known as viscosity parameter, and the critical compressibility factor z_c are defined as:

$$\xi = \frac{T_c^{1/6} R^{1/6} N_o^{1/3}}{M^{1/2} P_c^{2/3}} \quad \text{and} \quad z_c = \frac{P_c V_c}{R T_c} \quad (8a, b)$$

In the equation (8a,b), the units used are: R(universal gas constant)=8,314 [kJ kmol⁻¹ K⁻¹], N_o (Avogadro's number)=6.023 ·10²⁶ [kmol⁻¹], T_c [K], P_c [N m⁻²], M [kg kmol⁻¹], V_c [m³ kmol⁻¹] and ξ [(Pa s)⁻¹]. The critical properties and the factor ξ of these fluids used in this work, are listed in Table 5.

TABLE 5 : Thermophysical Data of R123, R134a and R142b

Substance	M [kg/kmol]	T _c [K]	p _c [Mpa]	ρ _c [kg/m ³]	z _c	ξ * 10 ⁻³ [Pas] ⁻¹
R123	152.9	456.94	3.674	550.00	0.2689	35.816
R134a	102.0	374.10	4.056	515.00	0.2597	39.721
R142b	100.5	410.20	4.124	435.05	0.2793	40.189

Finally, the viscosity at high pressure can be obtained from the residual viscosity $\Delta\eta$ and the zero - viscosity η_0 as follows:

$$\eta = \eta_0 + \Delta\eta \quad (9)$$

Fig. 10 shows the deviations of experimental viscosities of R123, R134a and R142b from the values computed with equations (7) to (9), in terms of the normalised density ρ/ρ_0 .

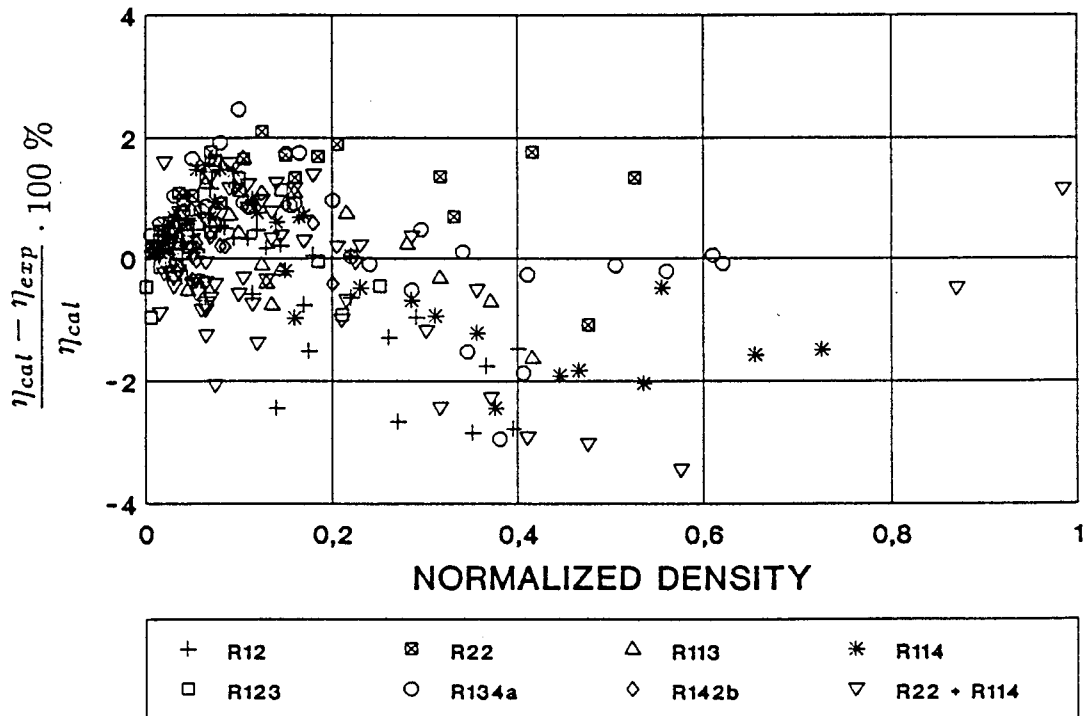


Fig. 10. Deviations of measured viscosities of refrigerants and their alternatives from the calculated values by equation (7) to (9)

For comparison, the viscosities of several other refrigerants and their mixtures from references (Nabizadeh and Mayinger 1989,1990) are also displayed in Fig. 10. Within the temperature and pressure ranges of our experimental data, the equations (7) to (9) represent the data largely within a tolerance of $\pm 2\%$ despite the polar nature of some substances. It is worth noting that these equations can also represent the viscosity values at saturation line with the same accuracy for temperatures below the reduced temperature, $T_r \leq 0.95$. Near the critical region, the experimental data, especially for some mixtures, deviate systematically from this correlation and tend to higher values.

4. Conclusion

The viscosity of the environmentally accepted refrigerants R123, R134a and R142b at low pressure can be represented, with the aid of Chapman - Enskog equation, with a mean deviation of $\pm 0.3\%$. At high pressure, the viscosity of these fluids reveals an anomalous behaviour, in which the viscosity decreases with increasing pressure. The inversion temperature at which this negative pressure effect inverts to a positive one lies, similar to the other refrigerants, at the reduced temperature $T_r = 0.78$. The viscosities of these fluids at moderate densities, $\rho < 300 \text{Kg/m}^3$, obey the law of corresponding states and can be represented by the same correlation, which was developed for the other refrigerants.

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