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Viscosity of gaseous mixtures of R22 + R142b

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ABSTRACT

New viscosity data of R22+R142b mixtures in the gas phase at concentrations 25, 50 and 75 wt% R22 are presented in this work. The viscosity has been measured in an oscillating- disk viscometer at temperatures from 30 to 100°C and in a pressure range of 0.1 to 3.5 MPa. The data were obtained relative to the viscosity of nitrogen. The accuracy of the data is estimated to be ±0.6%. Compared to our earlier results of non polar – non polar (R12+R114) and of polar – non polar (R22+R114) mixtures, the present data are characterized by some fluctuations at the intermediate densities along the isotherms 30 to 75°C , while at the isotherm 100°C this effect disappears. It is assumed that these fluctuations occur because of decomposition of the blend at lower temperatures.

1. INTRODUCTION

The mixtures of R22 and R142b, both environmentally acceptable refrigerants, have often been proposed as possible alternative candidates for R12. Following this proposal, more detail information is therefore needed to be able to make a final decision. On the other hand, R22 and R142b are both polar substances with the dipolmoments $\mu_{R22} = 1.5$ and $\mu_{R142b} = 2.1$ deby. Hence, it is expected that the properties of R22+R142b mixtures may reveal some peculiar deviations because of the polarity of both components. To ascertain this, investigations of these mixtures will be of great use to get knowledge about the behaviour of their properties. In continuation of our earlier investigations of the viscosity of several pure refrigerants and their mixtures, we present in this work the viscosity values of gaseous mixtures of R22+R142b. The experimental results of R12+R114, (non polar – non polar) and R22+R114, (polar – non polar) mixtures had been reported earlier (Nabizadeh and Mayinger 1989, 1990a). With respect to these results, it was possible to show that at moderate densities, $\varrho < 280$ kg/m^3, the residual viscosities of up to now investigated refrigerants and their mixtures reveal similar behaviour and obey the law of corresponding states. Consequently, it was possible to predict the residual viscosity of these substances, within a certainty of about ±2%, with the aim of a unified relationship. The measurements of the R22 + R142b mixtures should be used to verify if these also obey the general behaviour or ascertain their possible deviations against the other substances.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The measurements were carried out in the same oscillating-disk viscometer which was used for our earlier measurements. The basic principle of design, the characteristic of the suspension system and calibration of the viscometer have been described ealier (Nabizadeh and Mayinger 1989, 1990a). The conditions for an absolute measurement were not satisfied because of the design characteristic of the instrument and the relatively high density of the refrigerant in general. Therefore, the evaluation of the experiments was based on the relative method developed by Kestin, Leidenfrost, and Liu (1959) and Kestin and Witelaw (1963). The relative evaluation was done with respect to the viscosity data of nitrogen reported by Stephan, Krauss and Laesecke (1987). The measurements were performed at pressures ranging from 0.1 to 3.5 MPa and a temperature range of 30–100°C . The upper limit of 100°C was set with respect to the materials, mainly Pt, used in constructing the viscometer in order to avoid a possible thermal decomposition of the fluid. The measured viscosity values in this work are therefore limited only to the subcritical region. The mixtures were prepared by Kali-Chemie AG, Hannover, FRG. The densities of the mixtures were evaluated on the basis of experimental values reported by Yada, Kumagai and Watanabe (1989) and Huzhong et al. (1989).

The results of the measured viscosities of the binary mixtures R22+R142b at three concentrations of approximately 25, 50 and 75 wt% R22 are listed in tables 1, 2 and 3 respectively. The tables also contain the densities which were used for the evaluation of the experiments. Based on these densities the uncertainty of the viscosity values is extimated to be ±0.6%. Comparing the results of R22+R142b experiments with that of the mixtures of R12+R114 and R22+R114, the new results exhibit that this system is characterized by some special effects which were observed at athmospheric pressure as well as at high pressures. In the following discussion emphasis will be placed on these deviations.

TABLE 1

Viscosity of R22+R142b mixtures

R22+R142b (25 wt% R22)			
T [°C]	p [MPa]	ϱ [kg/m^3]	η [μPa s]
29.65	0.103	4.054	11.362
29.67	0.177	7.062	11.384
29.76	0.229	9.248	11.351
29.66	0.301	12.362	11.321
49.72	0.103	3.785	12.082
49.64	0.244	9.151	12.109
49.69	0.402	15.552	12.196
49.79	0.498	19.603	12.164
50.32	0.595	23.856	12.230
49.93	0.701	28.823	12.161
49.85	0.805	33.929	12.300
49.69	0.861	36.795	12.359
75.24	0.104	3.524	13.124
75.25	0.194	6.643	13.152
75.02	0.297	10.303	13.019
75.05	0.508	18.162	13.146
75.05	0.740	27.475	13.255
75.16	0.965	37.258	13.380
75.06	1.292	53.243	13.397
75.26	1.517	65.615	13.781
75.49	1.589	69.794	13.971
100.49	0.111	3.476	13.950
100.54	0.262	8.359	14.001
100.14	0.514	16.895	14.113
100.23	0.751	25.428	14.356
100.41	1.007	35.231	14.564
99.90	1.342	49.425	14.788
99.97	1.713	67.094	15.166
100.42	1.984	81.564	15.631
100.00	2.292	100.740	15.960
99.70	2.580	121.569	16.899

TABLE 2

R22+R142b (50 wt% R22)			
T [°C]	p [MPa]	ϱ [kg/m^3]	η [μPa s]
30.21	0.102	3.838	11.670
30.25	0.219	8.407	11.648
29.98	0.397	15.836	11.417
29.99	0.487	18.998	11.584
30.12	0.597	24.864	11.926
50.02	0.112	3.961	12.400
50.13	0.251	9.029	12.431
49.98	0.391	14.405	12.450
49.96	0.490	18.353	12.451
49.98	0.591	22.516	12.457
49.96	0.681	26.375	12.435
49.89	0.773	30.461	12.497
49.89	0.881	35.464	12.616
49.95	0.991	40.784	12.732
75.03	0.116	3.781	13.421
75.25	0.249	8.243	13.535
75.31	0.514	17.557	13.592
75.27	0.753	26.585	13.760
75.27	0.987	36.065	13.854
75.33	1.236	46.963	13.943
75.08	1.498	59.727	13.983
75.25	1.776	74.641	14.427
75.60	1.936	83.991	14.951
99.92	0.114	3.464	14.313
99.73	0.246	7.543	14.335
99.87	0.530	16.721	14.510
100.41	0.996	32.980	14.844
100.21	1.491	52.539	15.251
99.75	1.999	75.991	15.738
99.68	2.487	102.805	16.380
99.85	2.996	139.230	17.610

TABLE 3

Viscosity of R22+R142b mixtures

R22+R142b (75 wt% R22)			
T [°C]	p [MPa]	ϱ [kg/m^3]	η [μPa s]
29.79	0.107	3.871	12.177
29.86	0.231	8.536	12.144
29.91	0.368	13.912	12.166
29.96	0.492	19.034	12.248
29.96	0.597	23.542	12.238
30.00	0.692	27.831	12.279
50.07	0.103	3.492	12.970
50.09	0.114	7.240	12.971
50.18	0.364	12.740	12.956
49.94	0.534	19.137	12.956
49.98	0.665	24.332	13.063
50.17	0.818	30.657	13.167
49.62	0.951	36.566	13.192
50.49	1.108	43.622	13.316
75.53	0.118	3.682	13.925
75.71	0.366	11.732	13.994
75.54	0.647	21.399	14.073
75.60	0.996	34.388	14.271
75.56	1.128	39.720	14.334
75.61	1.155	40.796	14.389
75.71	1.223	43.510	14.530
75.56	1.259	45.192	14.434
75.64	1.297	46.742	14.375
75.54	1.399	51.282	14.485
75.63	1.489	55.120	14.592
75.61	1.716	65.852	14.657
75.66	1.997	80.424	15.071
75.95	2.168	89.976	15.471
100.22	0.116	3.378	14.815
100.24	0.251	7.385	14.814
100.41	0.528	15.895	14.926
100.06	0.985	30.961	15.164
100.03	1.493	49.483	15.586
100.24	2.001	70.419	16.111
100.10	2.499	94.325	16.784
100.11	2.985	120.683	17.802
100.20	3.172	133.142	18.329
100.45	3.383	148.308	19.118

2.1 VISCOSITY AT ATMOSPHERIC PRESSURE

Fig.1 represents the experimental viscosity values of R22+R142b mixtures at atmospheric pressure as a function of the mole fraction of R22. Each of the isotherms (30, 50, 75 and 100°C) has a turning point at composition of about 30% R22 which has only been observed in this system. It is difficult to explain this behaviour on the basis of the viscosity measurement only. But we suggest that besides the strong polarity of R142b, another possible explanation may be the existence of an azeotropic mixture around this composition.

The low pressure viscosity of R22, R142b and the binary mixtures of

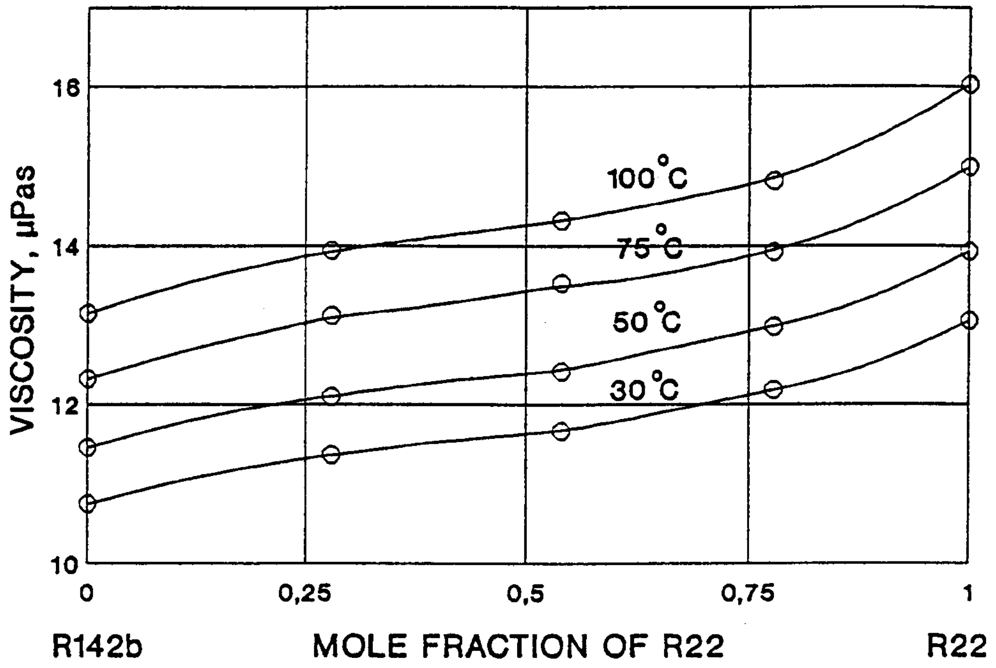

Fig. 1. Viscosity of R22+R142b mixtures at atmospheric pressure

R22+R114, reported by Nabizadeh and Mayinger (1990b,1990a), could be represented, despite the polar nature of the fluids, within their experimental accuracy by means of Chapman –Enskong equation on the basis of the universal collision integral proposed by Kestin, Ro and Wakeham (1972). For the binary mixtures the formula given by Hirschfelder, Curties and Bird (1966) was used. It was therefore reasonable to prove first the reliability of this evaluation method for predicting the viscosity of the new mixtures. To employ this method for the binary mixtures the interaction viscosity

$$\eta_{12} = \frac{5}{16} \cdot \left(kT \frac{2M_1 M_2}{M_1 + M_2} \right)^{1/2} \cdot \frac{1}{\sigma_{12}^2 \cdot \Omega_\eta(T^*)} \tag{1}$$

must first be estimated. T is Absolute temperature, $T^* = \mathrm{kT}/\epsilon_{12}$ is reduced temperature, M_1, M_2 are the molecular weight of the components 1 and 2 , k the Boltzmann's constant, σ_{12} and ε_{12} are the interaction parameters. The viscosity of binary mixtures is defined as follows:

$$\frac{1}{\eta_m} = \frac{X_\eta + Y_\eta}{1 + Z_\eta} \tag{2}$$

$$X_\eta = \frac{{y_1}^2}{\eta_1} + \frac{2y_1 y_2}{\eta_{12}} + \frac{{y_2}^2}{\eta_2} \tag{3}$$

$$Y_\eta = \frac{3}{5} {A_{12}}^* \left[\frac{{y_1}^2}{\eta_1} \left(\frac{M_1}{M_2} \right) + \frac{2 y_1 y_2}{\eta_{12}} \cdot \left[\frac{(M_1 + M_2)^2}{4 M_1 M_2} \right] \left(\frac{{\eta_{12}}^2}{\eta_1 \eta_2} \right) + \frac{{y_2}^2}{\eta_2} \left(\frac{M_2}{M_1} \right) \right] \tag{4}$$

$$Z_\eta = \tfrac{3}{5}A_{12}{}^{*}\left[y_1{}^2\left(\tfrac{M_1}{M_2}\right) + 2y_1y_2\left[\tfrac{(M_1+M_2)^2}{4M_1M_2}\left[\tfrac{\eta_{12}}{\eta_1} + \tfrac{\eta_{12}}{\eta_2} - 1\right]\right] + y_2{}^2\left(\tfrac{M_2}{M_1}\right)\right] \quad (5)$$

$$A_{12}^{*} = \frac{\Omega_\eta(T^*)}{\Omega_{D(T^*)}} \quad (6)$$

where, η_m is the mixture's viscosity, η_1, η_2 are the viscosities and y_1 and y_2 are the mole fractions of the pure components R22 and R142b respectively. The collision integrals $\Omega_\eta(T^*)$ and $\Omega_D(T^*)$ taken from (Kestin, RO, and Wakeham 1972) are defined as

$$\begin{aligned}\Omega_\eta(T^*) = exp[&0.45667 - 0.53955(lnT^*) + 0.187265(lnT^*)^2 - 0.03629(lnT^*)^3 \\ &+0.00241(lnT^*)^4] \quad (7)\\ \Omega_{D(T^*)} = exp&\left[0.347 - 0.444(lnT^*) + 0.093(lnT^*)^2 - 0.010(lnT^*)^3\right] \quad (8)\end{aligned}$$

The optimum values of σ_{12} and ε_{12}/k, based on the equations (7) and (8) and the procedure described by (Hirschfelder, Curtiss and Bird, 1966), were conversly evaluated from the best fit to our experimental data. For comparison these parameters were also evaluated with the collison integrals Ω_η and Ω_D which were obtained from the Stockmayer potential proposed by Monchick and Mason (1961) for the polar gases. The values of these parameters, estimated according to both evaluation methods, are listed in table 4.

TABLE 4

Scaling parameter σ_{12} and ϵ_{12}/k for R112+R142 mixtures
evaluated by potential integral of Kestin et al. and Monchidk and Mason.

Potential	Lennard–Jones		Stockmayer	
Ω_η, Ω_D	Kestin et al.		Monchick and Mason**	
Mixture	ϵ_{12}/k	$\sigma_{12}{}^*$	ϵ_{12}/k	σ_{12}
R22+R142b (25 wt% R22)	282.98	0.4960	282.98	0.4903
R22+R142b (50 wt% R22)	,,	0.5081	,,	0.5019
R22+R142b (75 wt% R22)	,,	0.5176	,,	0.5108
	$\sigma_{12}{}^* = 0.48407 + 0.04372 \cdot y_{R22}$,		** $\delta^*_{max} = 0.32$	
Mixing rules	$\sigma_{12} = \frac{1}{2} \cdot (\sigma_1 + \sigma_2)$,		$\sigma_{12} = 0.5007$ [nm]	
	$\epsilon_{12} = (\epsilon_1 \cdot \epsilon_2)^{\frac{1}{2}}$,		$\epsilon_{12}/k = 281.92$ [K]	

This table also contains the interaction parameters σ_{12} and ε_{12}/k which were calculated with the simple combination rules. Since the viscosity is less sensitive to the minor variation of ε_{12}/k, a constant value of ε_{12}/k has been used for all concentrations while the optimum values of σ_{12}, which secure the best representation of our experimental data, depend in this case on the concentration of the mixtures. Because the results obtained from both methods do not deviate from each other by more than 1.2%, we prefer to use equations (7) and (8) for further calculations. Fig.2 represents the deviations of the experimental data from the calculated values.

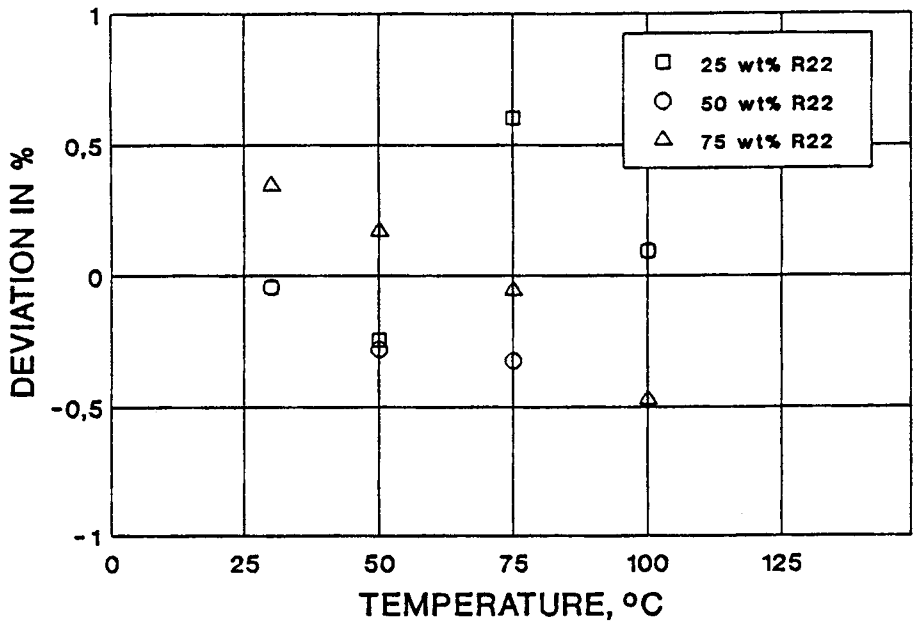

Fig. 2. Deviations of measured viscosity of R22+R142b mixtures from the calculated values by equations (3) to (8).

The maximum deviation of all measured data from the calculated ones amount to ±6%, while the mean deviation is only ±0.3%. It is worthnoting that the interaction parameters obtained with the combination rules represent the mixture viscosity of this system only at a composition of about 50 % with the same accuracy.

2.2 VISCOSITY AT HIGH PRESSURE

Fig.3 shows the viscosity of R22+R142b for a composition of 75wt% R22 along the nominal isotherms 30–100°C as a function of density. These values were obtained from the primary viscosity values by means of small corrections which, however, did not exceed 0.15%. In general, the behaviour of the

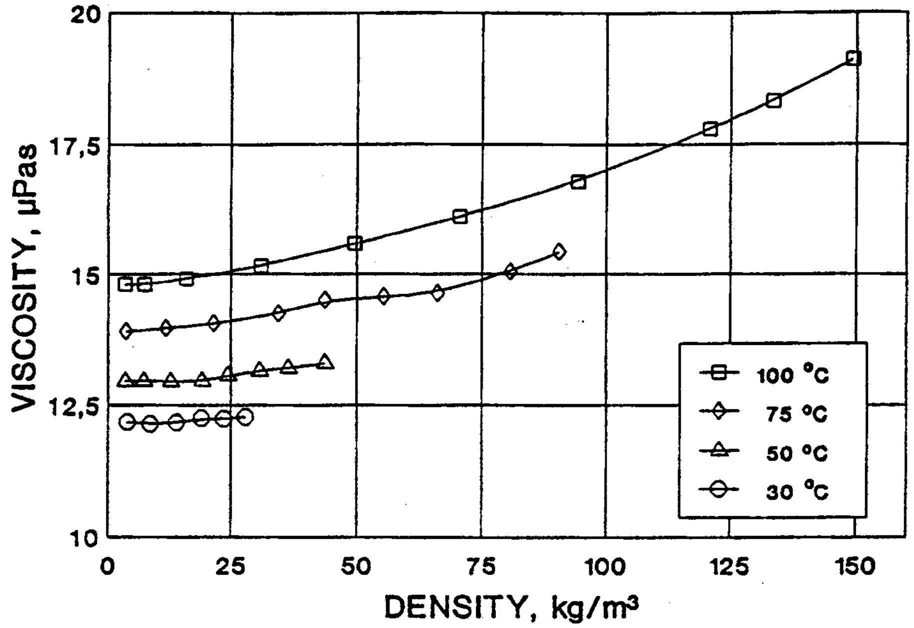

Fig. 3. Viscosity of R22+R142b mixtures as a function of the density at the concentration of 75 wt% R22.

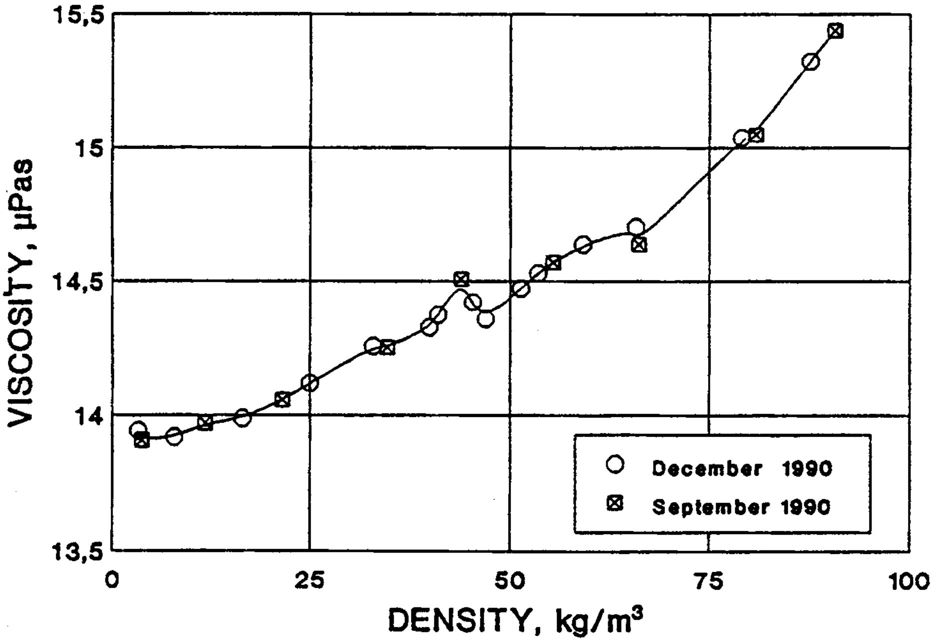

Fig. 4. Fluctuation of the viscosity of R22+R142b mixtures as a function of density at the isotherm 75°C and 75 wt% R22

viscosity of these mixtures is almost the same as that of the other already investigated refrigerants at a temperature of 100°C , while for the isotherms below 100°C the experimental data are associated with a kind of instability. Since this effect was first observed in R22+R142b mixtures, we remeasured one of the isotherms to assure the reproducibility of the values. Fig.4 shows the results of both measurements carried out in a time interval of about 3 months. This demonstrates that both sets of measurements are consistent and reproduceable. The maximum contribution to the base line viscosity amounts to about 1.4%. This observation is valid for all compositions investigated. Hence, we suggest that this might be due to the nature of the mixtures.

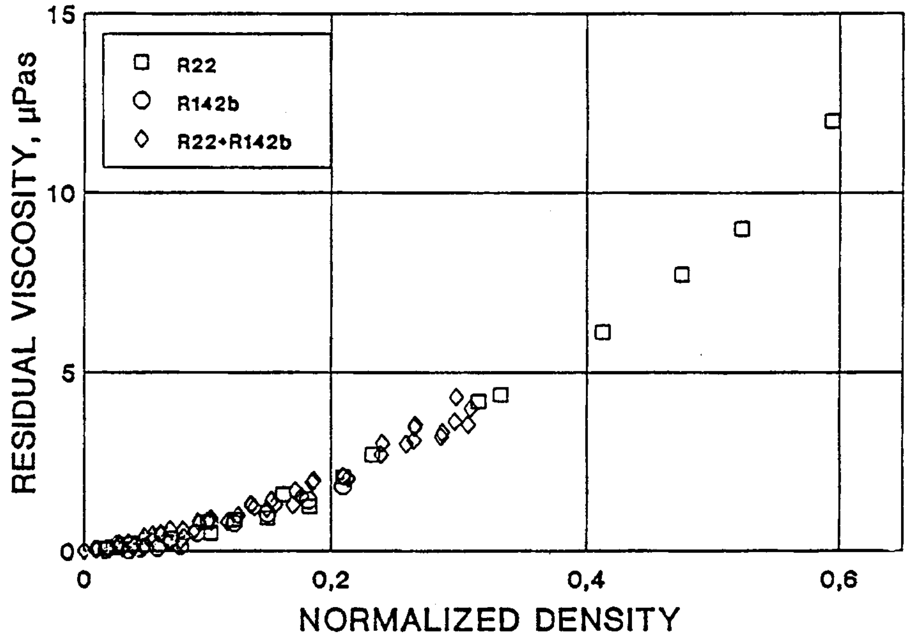

Fig. 5. Residual viscosity of R22, R142b and R22+R142b mixtures in terms of normalized density ϱ_{r0}.

The residual viscosity method, $\Delta\eta = \eta - \eta_0$, was used to predict the viscosity of R22+R142b mixtures at high pressures. This method was applicable for representing the viscosity of several other refrigerants and their mixtures. In order to improve also this method for the new data the residual viscosity was calculated using the experimental viscosity values at high pressures as well as at atmospheric pressure. The results are shown in Fig.5 in terms of the normalised density ϱ_{r_o} defined as:

$$\varrho_{r_0} = \frac{\varrho - \varrho_0}{\varrho_k} \tag{9}$$

where, ϱ is the density, ϱ_0 is the density at atmospheric pressure and ϱ_c is the critical density. For comparison, the residual viscosity of the pure components R22 and R142b, taken from our earlier work (Nabizadeh and Mayinger 1990a,1990b), are also displayed in Fig.5. It is obvious that within the experimental range of these measurements, $\varrho < 170\mathrm{kg}/m^3$, the residual viscosities of the mixtures of R22+R142b correspond to that of the pure components. Consequently, the following equation which was proposed for R22, R142b and several other refrigerants and their mixtures is also applicable for the present mixtures.

$$\Delta\eta\ \xi\ z_k = T_r^{-2.2}\left[ln\left(1.65 + \varrho_{r_0}^{0.8}\right)\right]^{1.6}\left[e^{(1-0.78/T_r)\varrho_{r_0}} - 1\right] \tag{10}$$

The factor ξ and the critical compressibility factor z_c are defined as:

$$\xi = \frac{T_c^{1/6} R^{1/6} N_o^{1/3}}{M^{1/2} P_c^{2/3}} \quad and \quad z_c = \frac{P_c V_c}{R\, T_c} \tag{11a, b}$$

In the equation (11a,b), the units used are: R=8,314 [kJ kmol^{-1} K^{-1}], N_o (Avogadro's number)=6.023 $\cdot 10^{26}$ [kmol^{-1}], T_c [K], P_c [N m^{-2}], M [kg kmol^{-1}], V_c [m^3 kmol^{-1}] and ξ [(Pa s)$^{-1}$]. The thermophysical properties taken from (Yada, Kumagai and Watanabe 1989) and the factor ξ of the fluids used in this work are listed in Table 5.

TABLE 5

Thermophysical Data and the factor ξ of R12+R142b mixtures

Substance	M [kg/kmol]	T_c [K]	p_c [Mpa]	ϱ_c [kg/m^3]	z_c	$\xi * 10^{-3}$ $[Pas]^{-1}$
R22+R142b (25 wt% R22)	96.58	399.98	4.365	456.95	0.2774	39.306
R22+R142b (50 wt% R22)	93.17	388.19	4.559	474.19	0.2775	38.682
R22+R142b (75 wt% R22)	89.60	378.44	4.753	491.40	0.2754	38.205

The absolute values of the viscosity at high pressure can then be calculated from the residual viscosity $\Delta\eta$ and the zero–viscosity η_0 as follows:

$$\eta = \eta_0 + \Delta\eta \tag{12}$$

Fig.6 shows the deviations of the measured viscosity values of R22+R142b mixtures from those computed with equations (10) to (12) in terms of the normalised density ϱ_{r0}. Within the temperature and pressure ranges of our

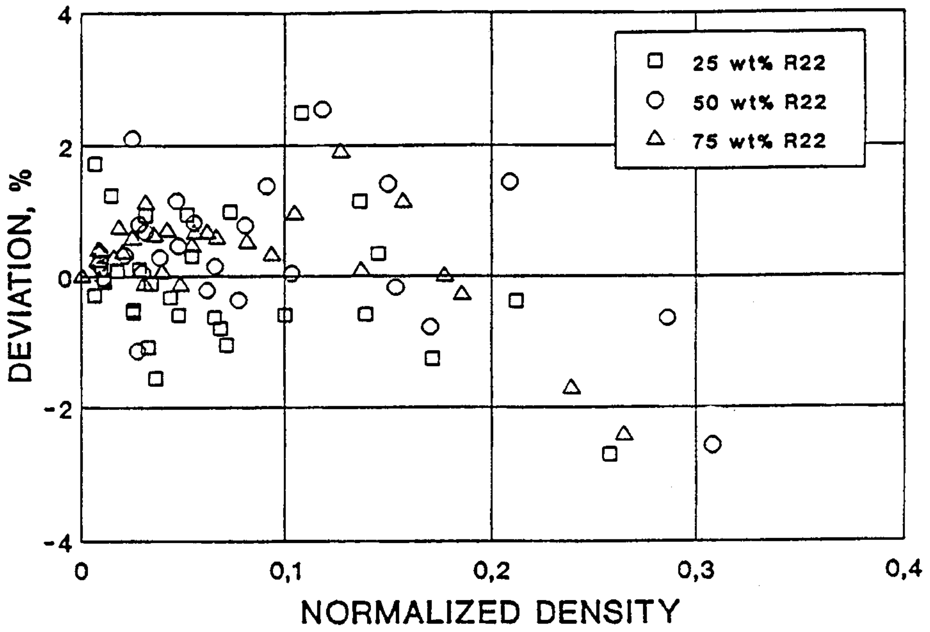

Fig. 6. Deviations of the measured viscosity of R22+R142b mixtures from the calculated values by equations (10) to (12).

experimental data, the proposed equations represent the data largely within a tolerance of ±2% despite the polar nature of both components.

3. CONCLUSION

The viscosity of R22+R142b mixtures follow almost the same behaviour similar to that of their pure components. In addition, this system is involved in some peculiar phenomenon most probably due to the nature of the system. The viscosity values at atmospheric pressure have a turning point at around a composition of 30%R22. Hence, it was not possible to handle these mixtures as homogeneous over the entire range of concentration. At intermediate densities, the experimental values along the isotherms lower than 100°C indicate an instable behaviour which might be caused by the decomposition of the blend in this region.

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