VISCOSITY OF BINARY GASEOUS MIXTURES
OF FLUOROCARBONS

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Viscosity of eight binary gaseous mixtures consisting of fluorocarbon refrigerants, namely
R290 mixtures: R290+R22, R290+R115, R290+R502
R22 mixtures: R22+R12, R22+R13, R22+R13B1, R22+R14, R22+R152a
have been measured at temperatures from 298 to 348 K at atmospheric pressure. The measurements were
performed by a rolling-ball viscometer, which was calibrated using nitrogen as a standard gas. The uncertainty of
the viscosity data obtained is estimated to be within ±1.0%.
   The visocsity of all gaseous mixtures investigated changes almost linearly with composition at constant
temperature. The experimental data could be expressed by the empirical Sutherland equation with mean deviation
of 0.36%. It was found that the Chapman-Enskog theory reproduced the experimental data with mean deviations
within 1% except for R290+R502 mixtures.

1. Introduction

1. Introduction of the important thermophysical properties used as fundamental data not only for process design in chemical engineering but also for the interpretation of molecular interactions in modern kinetic theory. Recently, fluorocarbon refrigerants and their mixtures have been noticed with keen interest as promising working fluids in the various energy systems that use low-quality energy sources, such as solar, geothermal, ocean thermal and industrial waste energy sources. Therefore, accumulation of accurate thermophysical property data is desirable, especially for nonazeotropic mixtures.

In the present work, the viscosities of eight binary gaseous mixtures made from R12 (CCl_2F_2), R13 ($CClF_3$), R14 (CF_4), R13B1 ($CBrF_3$), R22 ($CHClF_2$), R115 ($CClF_2CF_3$), R152a (CH_3CHF_2), R290 (C_3H_8) and R502 (mixture of 48.8 wt% R22 and 51.2 wt% R115) were measured at temperatures from 298 to 348 K at atmospheric pressure. Measurements were performed by a rolling-ball viscometer on a relative basis with respect to the viscosity of nitrogen. The uncertainty of the present measurements was estimated to be within ±1.0%. The experimental data are compared with values calculated by the rigorous theory of Chapman-Enskog and other empirical methods.

2. Experimental

Viscosity was measured by a rolling-ball viscometer. The apparatus and experimental procedure were almost the same as those in previous works.[21] In this method the viscosity is determined from the rolling velocity of a steel ball in an inclined Pyrex glass tube filled with a sample fluid. The rolling time was measured within ±0.1 ms by two sets of electromagnetic induction coils and an electronic time-interval counter. The temperature of the viscometer was maintained constant within ±0.03 K in a liquid thermostat. The pressure was measured by Heise Bourdon gauges calibrated against a dead-weight gauge. The uncertainty of the pressure measurement was within ±0.1%. The viscometer was calibrated up to 1.5 MPa at each temperature using nitrogen, whose standard values were obtained from Hanley *et al.*[4] for viscosity and Jacobsen *et al.*[8] for density. Sample gases were obtained from commercial sources: nitrogen was supplied by Teikoku Sanso Co., Ltd., propane by Seitetsu Kagaku Co., Ltd. and fluorocarbons by Daikin Industries Ltd. Their purities were better than 99.5%. The sample gases were used without further purification.

The densities of sample gases were calculated by the equations of state.[1] The compositions of gaseous mixtures were calculated by the partial pressures and

the equations of state since the pressure was low in this work. For several mixtures the compositions were also determined by gas chromatography. Results by the two methods, agreed well within 0.005 mole fraction. The imprecision in these measurements of viscosity was within $\pm 0.5\%$, considering the uncertainties of temperature, pressure, composition, rolling time and calibration of viscometer. Since the uncertainty of the viscosity values of nitrogen as the reference gas are estimated to be within 0.5%, the uncertainty of the final values of viscosity is less than $\pm 1.0\%$.

3. Experimental Results

The experimental results are shown in **Table 1**. Although the mixture of R290 + R502 is a ternary system, this system was treated as a pseudo-binary mixture in the present work because R502 has a constant composition.

3.1 Comparison with literature values

To confirm the reliability of the present measurements the experimental data of pure components and mixtures were compared with literature values.[9,20] As for R290, R22, R115, R12, R13 and R14, the experimental results agree with reliable evaluated values within $\pm 1.5\%$. For R502 and R152a, one set of experimental data each is available in the literature[13,14] and the present results are consistent with them within $\pm 1\%$. For R13B1, reliable experimental data are scarce. Those of Karbonov et al.[10] by a capillary viscometer deviate from earlier experimental results by the rolling-ball method[20] by 6%. The present data are found to give an average deviation of +2% from the former and of -2.5% from the latter.

Regarding the viscosity of the gaseous mixtures investigated, literature values are quite scarce. So far as we know about binary systems, we can find only two sets of experimental data, those of Schrichand et al.[12] for R22 + R12 and Takahashi et al.[17] for R22 + R152a. The data of Takahashi et al. can be compared directly with our results for R22 + R152a at 298 K. They agree well within $\pm 1\%$. The data of Srichand et al. show also a composition dependence quite similar to our results, although their data cannot be compared directly with those in this work because of a small difference of temperature.

3.2 Composition dependence of viscosity

The composition dependence of the viscosity is illustrated for mixtures of R290 and R22 in **Figs. 1** and **2**, respectively. In all mixtures, the viscosity changes almost linearly with composition and has no definite maximum or minimum throughout the whole range of composition. However, the viscosity of mixtures cannot be calculated rigorously by the simple mole fraction average method which follows:

Table 1. Viscosity data of fluorocarbon refrigerants mixtures

(In micro Pa·s)					
x_{R290}	η	x_{R290}	η	x_{R290}	η
R290 Mixtures					
R290 + R22		R290 + R115		R290 + R502	
$T = 298.15$ K		$T = 298.15$ K		$T = 298.15$ K	
0.000	12.96	0.000	12.62	0.000	12.93
0.149	12.42	0.143	12.36	0.148	12.43
0.325	11.68	0.317	11.55	0.321	11.88
0.503	10.87	0.497	11.11	0.502	10.82
0.681	10.04	0.678	10.21	0.680	10.09
0.854	9.21	0.853	9.37	0.862	9.20
1.000	8.31	1.000	8.31	1.000	8.31
$T = 323.15$ K		$T = 323.15$ K		$T = 323.15$ K	
0.000	13.89	0.000	13.41	0.000	13.85
0.149	13.28	0.144	13.07	0.148	13.35
0.323	12.63	0.316	12.61	0.322	12.65
0.508	11.60	0.498	11.68	0.504	11.91
0.686	10.70	0.677	10.90	0.680	10.86
0.852	9.97	0.851	9.98	0.853	10.05
1.000	8.97	1.000	8.97	1.000	8.94
$T = 348.15$ K		$T = 348.15$ K		$T = 348.15$ K	
0.000	14.75	0.000	14.36	0.000	14.72
0.149	14.18	0.150	13.95	0.148	14.23
0.321	13.37	0.310	13.50	0.320	13.66
0.500	12.65	0.492	12.65	0.504	12.86
0.653	11.73	0.684	11.73	0.672	11.67
0.851	10.54	0.844	10.77	0.852	10.71
1.000	9.64	1.000	9.64	1.000	9.64

| x_{R22}	η	x_{R22}	η	x_{R22}	η
R22 Mixtures					
R22 + R12		R22 + R13		R22 + R152a	
$T = 298.15$ K		$T = 298.15$ K		$T = 298.15$ K	
0.000	12.34	0.000	14.36	0.000	10.41
0.248	12.51	0.353	13.83	0.263	10.98
0.402	12.61	0.669	13.37	0.524	11.56
0.619	12.71	1.000	12.85	0.773	12.23
0.758	12.79	$T = 323.15$ K		1.000	12.85
1.000	12.85	0.000	15.44		
$T = 323.15$ K		0.227	15.05		
0.000	13.39	0.388	14.82	$T = 323.15$ K	
0.247	13.52	0.605	14.47	0.000	11.22
0.517	13.68	0.729	14.30	0.261	11.76
0.759	13.81	0.858	14.10	0.527	12.51
1.000	13.87	1.000	13.87	0.759	13.14
R22 + R13B1		R22 + R14		1.000	13.87
$T = 298.15$ K		$T = 298.15$ K			
0.000	15.18	0.000	17.23		
0.164	14.91	0.168	16.65		
0.314	14.62	0.367	15.94		
0.517	14.25	0.511	15.28		
0.689	13.82	0.674	14.57		
0.852	13.35	0.834	13.73		
1.000	12.85	1.000	12.85		
$T = 323.15$ K		$T = 323.15$ K			
0.000	16.21	0.000	18.51		
0.181	15.91	0.164	17.92		
0.347	15.63	0.322	17.13		
0.521	15.29	0.522	16.43		
0.660	14.81	0.677	15.75		
0.843	14.37	0.840	14.84		
1.000	13.87	1.000	13.87		
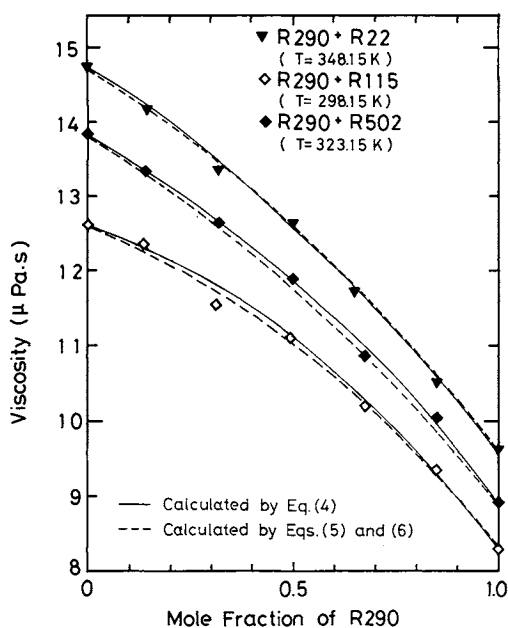
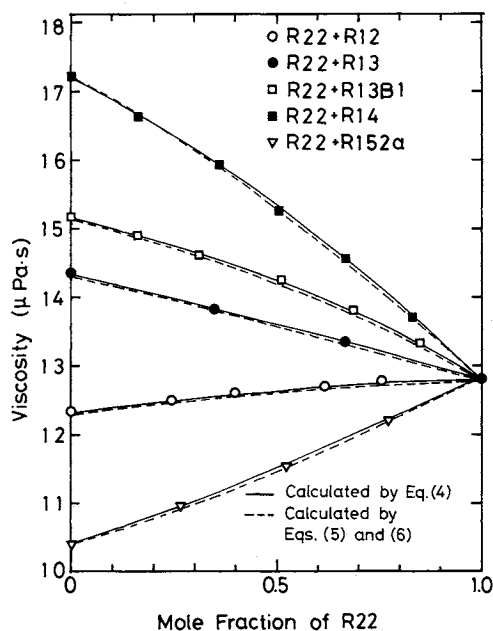Fig. 1. Composition dependence of viscosity for R290 mixtures.

Fig. 2. Composition dependence of viscosity for R22 mixtures at 298.15 K.

$$\eta_m^{add} = x_1\eta_1 + x_2\eta_2 \qquad (1)$$

where η_1 and η_2 are viscosities of pure components, and x_1 and x_2 their mole fractions. The experimental viscosity value η_m^{exp} tends to be somewhat larger than the calculated viscosity η_m^{add}.

To compare the deviations from Eq. (1), two kinds of excess viscosities η^E and η^{PE} are defined:

$$\eta^E = \eta_m^{exp} - \eta_m^{add} \qquad (2)$$

$$\eta^{PE} = \eta^E/\eta_m^{add} \times 100 \qquad (3)$$

The percent excess viscosities are illustrated in **Fig. 3**. Those of mixtures containing R290 are generally larger than those of fluorocarbon mixtures of R22. Among the fluorocarbon mixtures, the percent excess viscosities of R22+R14 and R22+R13B1 are comparatively larger than in other systems. On the other hand, the percent excess viscosity of R22+R13 system is less than $\pm 0.2\%$. The simple mole fraction average method is generally usable in this system. For R22+R152a system alone the excess viscosity is negative.

3.3 Correlation by Sutherland equation

At constant temperature under atmospheric pressure, the composition dependence of the viscosity for binary gaseous mixtures can be expressed by the Sutherland equation,[11]

$$\eta_m = \frac{\eta_1}{1 + \phi_{12}(x_2/x_1)} + \frac{\eta_2}{1 + \phi_{21}(x_1/x_2)} \qquad (4)$$

where ϕ_{12} and ϕ_{21} are characteristic combination factors of the mixture. The viscosity of a mixture η_m at any composition can be calculated by this equation, using the viscosities of pure components, when the combination factors are evaluated in advance by some methods. In this work the optimum values of the combination factors were determined by the nonlinear regression method of least squares on the basis of experimental results. The combination factors determined are summarized in **Table 2**, together with the mean and maximum deviations from the experimental data. The Sutherland equation can reproduce the experimental data with a mean deviation of 0.36% and a maximum deviation of 1.35%. The solid lines in Figs. 1 and 2 are values calculated by Eq. (4).

3.4 Estimation by Chapman-Enskog theory

The viscosity of dilute gases and their mixtures can be calculated by the Chapman-Enskog theory.[5] In this work, the viscosity of gaseous mixture was calculated by this theory and compared with experimental data. The theory can be summarized by the following equations:

$$\eta_m = f(x_1, x_2, M_1, M_2, \eta_1, \eta_2, \eta_{12}) \qquad (5)$$

$$\eta_{12} = g(\varepsilon_{12}, \sigma_{12}, M_1, M_2, T) \qquad (6)$$

where M_1 and M_2 are molecular weights and η_{12} an interaction viscosity, ε_{12} and σ_{12} are the force constant between unlike molecules and are calculated by an empirical method as follows:[11]

$$\varepsilon_{12} = (\varepsilon_1 \cdot \varepsilon_2)^{1/2} \qquad (7)$$

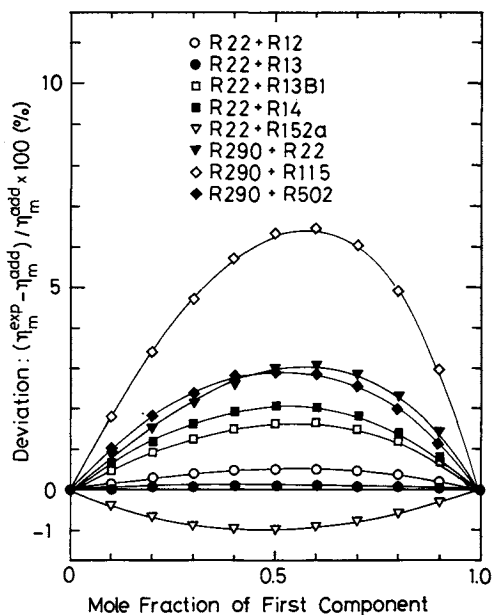$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \qquad (8)$$

Fig. 3. Composition dependence of percent excess viscosity at 298.15 K.

Table 3. Force constants of refrigerants

Refrigerant	Potential	ε/k [K]	σ [nm]	Ref.
R290	*L-J	206.0	0.5240	11
R22	L-J	214.8	0.4971	15
	**S	261.0	0.471	7
R12	L-J	274.0	0.516	2
R13	L-J	204.0	0.4971	16
R13B1	L-J	246.7	0.5014	18
R14	L-J	134.0	0.4662	11
R115	L-J	201.9	0.5876	19
R152a	L-J	442.1	0.4321	14
R502	L-J	227.6	0.5241	***13

* L-J, Lennard-Jones (12-6) potential. ·
** S, Stockmayer (12-6-3) potential.
*** Calculated from the viscosity of ref. 13.

relatively small. On the other hand, the force constants for R290+R22 and R22+R14, which consist of strongly polar and nonpolar molecules, were calculated by the combination rule proposed by Hongo et al.[6]

$$\sigma_{12}=(\sigma_p+\sigma_n)/2 \cdot \mathit{\Lambda}^{-1/6} \qquad (9)$$

$$\varepsilon_{12}=(\varepsilon_p\cdot\varepsilon_n)^{1/2}\cdot \mathit{\Lambda}^2/(Z_{cn}^{1/2}+Z_{cp}^{1/2})^2 \qquad (10)$$

$$\mathit{\Lambda}=1+\frac{1}{4}\frac{\alpha_n}{\sigma_n^3}\frac{\mu_p^2}{\varepsilon_p\sigma_p^3}\sqrt{\frac{\varepsilon_p}{\varepsilon_n}} \qquad (11)$$

where Z_{cp} and Z_{cn} are the critical compressibility factors of polar and nonpolar substances, μ_p a dipole moment of polar molecule and α_n a polarizability of nonpolar molecule.

ε_p and σ_p are the force constants of Stockmayer (12-6-3) potential for polar molecule, and ε_n and σ_n are those of Lennard-Jones (12-6) potential for nonpolar molecule.

For R22+R152a system, which consists of strongly polar molecules, the interaction viscosity was calculated with the correction of polarity and molecular shape proposed by Chung et al.[3] as follows:

$$\eta_{12}'=\eta_{12}\{1-(0.2756\omega_{12}-0.059035\mu_{12}^{*4})\} \qquad (12)$$

where ω is Pitzer's acentric factor and μ^* the reduced dipole moment, that is, $\mu^*=\mu/(\varepsilon\cdot\sigma^3)^{1/2}$.

ω_{12} and μ_{12}^* were calculated as follows:

$$\omega_{12}=(\omega_1+\omega_2)/2 \qquad (13)$$

$$\mu_{12}^*=(\mu_1^*\cdot\mu_2^*)^{1/2} \qquad (14)$$

The interaction viscosity η_{12} was thus obtained for each system. The calculated viscosities by Eqs. (5) and (6) are compared with the experimental data in **Table 4**. For all systems except R290+R502 at 348 K, the mean deviation is within $\pm1\%$ and the maximum deviation within $\pm2\%$. The dotted lines in Figs. 1 and 2 are calculated values thus obtained.

Table 2. Coefficients of Sutherland equation

System	Temp. [K]	ϕ_{12}	ϕ_{21}	Mean dev. [%]	Max. dev. [%]
R290+R22	298.15	1.212	0.802	0.37	0.59
	323.15	1.121	0.850	0.69	1.07
	348.15	0.742	1.088	0.44	0.90
R290+R115	298.15	1.716	0.581	0.81	1.35
	323.15	0.840	0.941	0.47	0.96
	348.15	0.991	0.835	0.23	0.43
R290+R502	298.15	0.814	1.035	0.79	1.28
	323.15	1.268	0.743	0.50	1.17
	348.15	0.759	1.021	0.63	1.06
R22+R12	298.15	1.216	0.798	0.05	0.09
	323.15	1.980	0.485	0.11	0.14
R22+R13	298.15	1.071	0.937	0.06	0.07
	323.15	1.011	0.995	0.09	0.14
R22+R13B1	298.15	1.668	0.607	0.12	0.18
	323.15	0.870	1.062	0.23	0.43
R22+R14	298.15	0.938	0.975	0.14	0.17
	323.15	1.475	0.702	0.47	0.76
R22+R152a	298.15	1.454	0.657	0.10	0.15
	323.15	1.841	0.492	0.22	0.27

The force constants based on Lennard-Jones (12-6) potential were cited from the literature for pure components except R502, for which hypothetical force constants were calculated from the experimental viscosity data of Takahashi et al.[13] The force constants adopted are listed in **Table 3**.

For the systems of R290+R115, R290+R502, R22+R12, R22+R13, and R22+R13B1, the force constants were obtained by Eqs. (7) and (8) because the difference of polarity between component gases is

Table 4. Results of prediction of viscosity by Chapman-Enskog theory

System	Temp. [K]	Mean dev. [%]	Max. dev. [%]
R290 + R22	298.15	0.429	0.802
	323.15	0.787	1.301
	348.15	0.444	0.661
R290 + R115	298.15	0.825	1.421
	323.15	0.707	1.328
	348.15	0.263	0.579
R290 + R502	298.15	0.793	1.458
	323.15	0.978	1.978
	348.15	1.214	2.488
R22 + R12	298.15	0.269	0.327
	323.15	0.163	0.303
R22 + R13	298.15	0.240	0.306
	323.15	0.105	0.170
R22 + R13B1	298.15	0.388	0.647
	323.15	0.228	0.471
R22 + R14	298.15	0.315	0.603
	323.15	0.642	1.121
R22 + R152a	298.15	0.733	0.817
	323.15	0.392	0.740

Conclusion

The viscosities of eight binary gaseous mixtures of fluorocarbons were measured at temperatures from 298 to 348 K at atmospheric pressure. The composition dependence of the viscosity can be well correlated by the Sutherland equation when the optimum values of the combination factors were determined on the basis of the experimental data.

Among various theoretical or empirical estimation methods for viscosity of gaseous mixtures, the Chapman-Enskog theory is found to predict the present experimental data most successfully, with mean deviations within 1%.

Nomenclature

k	= Boltzman constant	$[1.308622 \times 10^{-23} \mathrm{J \cdot K^{-1}}]$
M	= molecular weight	$[\mathrm{g \cdot mol^{-1}}]$
T	= temperature	$[\mathrm{K}]$
x	= mole fraction	[—]
Z_C	= compressibility factor at critical point	[—]
α	= polarizability	$[\mathrm{m^3}]$
ε	= force constant of energy	$[\mathrm{J}]$
η	= viscosity	$[\mathrm{Pa \cdot s}]$
Λ	= correction term of Eq. (11)	[—]
μ	= dipole moment	$[\mathrm{C \cdot m}]$
σ	= force constant of distance	$[\mathrm{m}]$
ϕ	= combination factor of Eq. (4)	[—]
ω	= Pitzer's acentric factor	[—]

⟨Subscripts⟩
m   = mixture

n   = nonpolar molecule
p   = polar molecule

⟨Superscripts⟩
add   = simple mole fraction average
E   = excess
exp   = experimental
PE   = percent excess

Literature Cited

1) American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc.: "Thermophysical Properties of Refrigerants," New York (1976).
2) Bishop, P. J.: M. S. thesis (Purdue University, 1972).
3) Chung, T., L. L. Lee and K. E. Starling: *Ind. Eng. Chem., Fundam.*, **23**, 8 (1984).
4) Hanley, H. J. M., R. D. McCarty and W. M. Haynes: *J. Phys. Chem. Ref. Data*, **3**, 979 (1974).
5) Hirschfelder, J. O., C. F. Curtiss and R. B. Bird: "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York (1954).
6) Hongo, M. and H. Iwasaki: *Rev. Phys. Chem. Japan*, **48**, 1 (1978).
7) Hongo, M. and S. Takahashi: *J. Chem. Eng. Japan*, **15**, 155 (1982).
8) Jacobsen, R. T. and R. B. Stewart: *J. Phys. Chem. Ref. Data*, **2**, 757 (1973).
9) Japan Society of Mechanical Engineering: "Thermophysical Properties of Fluids," Tokyo (1983).
10) Karbanov, E. M. and V. Z. Geller: *Neft. Gazov Promst.*, **11**, 22 (1974).
11) Makita, T.: "Viscosity and Thermal Conductivity," Baifukan, Tokyo (1975).
12) Srichand, M., M. A. Tirunarayan and A. Ramachandran: *ASHRAE J.*, **12**, 61 (1970).
13) Takahashi, M. and H. Iwasaki: Preprint of the 15th High Pressure Conference of Japan, p. 57 (1973).
14) Takahashi, M. and S. Takahashi: Preprint of the 23rd High Pressure Conference of Japan, p. 208 (1982).
15) Takahashi, M., S. Takahashi and H. Iwasaki: *Kagaku Kogaku Ronbunshu*, **9**, 482 (1983).
16) Takahashi, M., S. Takahashi and H. Iwasaki: *J. Chem. Eng. Data*, **30**, 10 (1985).
17) Takahashi, M., C. Yokoyama and S. Takahashi: Preprint of the 18th Autumn Meeting of the Society of Chemical Engineers of Japan, p. 446 (1983).
18) Takahashi, M., C. Yokoyama and S. Takahashi: Preprint of the 25th High Pressure Conference of Japan, p. 262 (1984).
19) Takahashi, M., C. Yokoyama and S. Takahashi: *Kagaku Kogaku Ronbunshu*, **11**, 155 (1985).
20) Tanaka, Y.: *Refrigeration*, **52**, 34 (1977).
21) Tanaka, Y., H. Kubota, T. Makita and H. Okazaki: *J. Chem. Eng. Japan*, **10**, 83 (1977).