Viscosity of Gaseous Mixtures of Methoxymethane + Nitrogen

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This paper reports experimental results for the viscosity of gaseous mixtures of methoxymethane + nitrogen. The measurements were carried out with an oscillating-disk viscometer of the Maxwell type at temperatures from (298.15 to 423.15) K and at pressures up to 4.97 MPa. The viscosity at 0.1 MPa was found to be correlated with a maximum deviation of 1.7 % and average deviation of 0.9 % by the Chapman−Enskog equation. An empirical equation was obtained for the viscosity as a function of composition, temperature, and density. This equation reproduced the observed viscosity with a maximum deviation of 3.8 % and an averaged deviation of 0.7 %.

1. Introduction

Recently, the methoxymethane and nitrogen mixture has attracted considerable attention for application as a propellant alternative to hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). In addition, as methoxymethane is considered to be used for automotive fuel, the fuel−air mixing process of high-speed methoxymethane sprays is very important. In the optimum design of these processes, the thermophysical properties of methoxymethane and the methoxymethane + nitrogen mixture are indispensable. The viscosity of gases, like thermal conductivity and diffusion coefficient, is an important thermophysical property in chemical engineering and in molecular physics. Accurate experimental data of the gas viscosity are used to obtain information about intermolecular forces and more practically to design unit operations in chemical engineering. The viscosity of methoxymethane at saturated conditions was reported by Wu et al.[1] Sivebaek et al. investigated the viscosity of methoxymethane at 25 °C and the effect of gases on the viscosity of methoxymethane.[2,3] However, gaseous viscosities of methoxymethane and the methoxymethane + nitrogen mixture over a wide temperature range have not been reported yet.

In our previous studies, we measured the gaseous viscosity of the polar−nonpolar mixtures.[4−8] In this paper, viscosities of gaseous mixture of methoxymethane + nitrogen were measured with an oscillating-disk viscometer of the Maxwell type. The experimental temperature ranges were from (298.15 to 423.15) K, and pressures were up to 4.97 MPa.

2. Experimental

The viscosity was measured with an oscillating disk viscometer of the Maxwell type. The gas density was measured with a high-pressure gas pipet. The experimental apparatus and procedure were essentially the same as those described in previous studies.[9,10] The apparatus constant at the experimental temperature and pressure conditions was determined by considering the viscosity data of nitrogen taken from Stephan et al.[11] and the nitrogen gas density data from Jacobsen and Stewart.[12] The compositions of the sample mixtures were determined by gas chromatography. Temperature and pressure values have an uncertainty of ± 0.01 K and ± 0.5 kPa. The uncertainty of the composition determination was estimated to be less than 10^{-3} mole fraction. Density values have an uncertainty of ± 0.3 %. The estimated uncertainty of the present viscosity data is within ± 0.5 %.

The methoxymethane which had a stated purity of 99.0 % was supplied from Tokyo Chemical Industry Co., Ltd. The sample was purified by distillation several times. The nitrogen which had a stated purity of 99.99 % was supplied from Nippon Sanso Co., Ltd. The sample was used without further purification.

3. Results and Discussion

The experimental results for the viscosity of the methoxymethane + nitrogen system are presented in Table 1. Figure 1 shows the deviations of the experimental viscosity data of nitrogen from the literature values.[13] As shown in Figure 1, the present results for the viscosity of nitrogen at 0.1 MPa agree well with those of Seibt et al. Figures 2 and 3 show the viscosity of methoxymethane + nitrogen mixtures at 323.15 K. A negative initial slope of the viscosity isotherm, $(\partial\eta/\partial P)_T$, for methoxymethane changes sign as the concentration of nitrogen increases. The viscosity at 0.1 MPa was compared with the one calculated by the Chapman−Enskog equation derived from the kinetic theory for dilute gases

$$\eta°/\mu\text{Pa·s} = 2.6695 \cdot \frac{(MT/\text{K})^{1/2}}{\sigma^2\Omega^*} \tag{1}$$

where M is the molecular weight; T is the temperature; σ is a length scaling factor; and Ω^* is a reduced collision integral. For nitrogen, the Lennard−Jones potential was applied. Neufeld et al. developed an empirical correlation for the temperature dependencies of the transport collision integrals of the Lennard−Jones 12-6 potential, which represent Ω^* in terms of the reduced temperature $T^* = k(T/\text{K})/\varepsilon$ in the range from 0.3 to 100 with an uncertainty of 0.1 %.[14] The correlation of Neufeld et al. for the reduced collision integral Ω^* is as follows

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Table 1. Experimental Viscosity for the Methoxymethane (1) + Nitrogen (2)

T		P	ρ	η	T		P	ρ	η	T		P	ρ	η
K	x_1	MPa	(kg·m^{-3})	(μPa·s)	K	x_1	MPa	(kg·m^{-3})	(μPa·s)	K	x_1	MPa	(kg·m^{-3})	(μPa·s)
298.15	0	0.101	1.178	17.86	373.15	0	0.101	0.633	21.16		1	0.101	0.948	12.34
		0.240	2.833	17.88			0.495	4.527	21.21			0.300	4.392	12.37
		0.672	7.705	17.94			1.000	8.832	21.26			0.531	7.678	12.39
	0.256	0.101	1.178	14.83			2.006	18.01	21.40			0.992	15.10	12.44
		0.305	4.298	14.88			2.930	26.15	21.52			2.085	34.47	12.74
		0.683	9.296	14.94			3.985	35.64	21.68			2.985	54.66	13.17
	0.449	0.101	1.433	13.00			4.966	44.70	21.84			3.965	87.68	14.10
		0.264	4.075	13.00		0.281	0.101	0.665	17.73			4.480	112.3	15.04
		0.640	9.965	13.03			0.325	3.419	17.77			4.620	122.4	15.43
	0.752	0.101	1.783	10.63			0.520	5.508	17.77	423.15	0	0.101	0.568	23.18
		0.262	4.839	10.60			1.011	10.64	17.84			0.550	4.226	23.22
		0.614	11.78	10.60			1.915	20.80	18.01			1.032	8.294	23.28
	1	0.101	1.910	9.22			3.005	33.02	18.23			2.012	15.86	23.38
		0.296	6.081	9.18		0.522	0.101	0.950	15.34			3.435	26.90	23.54
		0.475	10.06	9.10			0.301	3.577	15.35			4.832	37.69	23.73
323.15	0	0.101	0.858	19.01			0.530	6.584	15.39		0.272	0.101	0.662	19.78
		0.290	3.114	19.04			1.029	12.76	15.50			0.314	2.901	19.84
		0.466	4.925	19.06			2.036	25.83	15.68			0.529	4.699	19.86
		0.856	9.024	19.11			3.065	40.84	15.99			1.040	9.555	19.94
	0.228	0.101	1.080	16.29		0.820	0.101	1.171	12.82			2.030	18.92	20.08
		0.354	4.544	16.32			0.312	4.400	12.85			2.955	27.91	20.18
		0.553	6.768	16.36			0.516	7.217	12.85			4.000	37.87	20.38
		0.910	11.15	16.36			1.038	15.16	12.95			4.911	46.70	20.57
	0.449	0.101	1.144	14.02			1.952	30.93	13.14		0.527	0.101	0.694	17.21
		0.321	4.449	14.06			2.895	51.12	13.52			0.316	3.343	17.23
		0.486	6.864	14.08		1	0.101	1.235	11.61			0.505	5.456	17.26
		0.714	10.20	14.08			0.305	4.748	11.60			1.047	11.35	17.34
		0.990	13.89	14.13			0.500	7.787	11.62			2.013	22.17	17.53
	0.698	0.101	1.303	12.00			1.028	16.71	11.68			2.995	33.84	17.69
		0.270	4.353	12.01			1.940	35.33	11.91			3.973	45.63	17.96
		0.485	7.499	12.01			2.505	51.25	12.19			4.873	56.58	18.22
		0.695	11.57	12.06			2.875	67.49	12.47		0.764	0.101	1.072	15.16
		0.946	15.73	12.08			3.049	74.07	12.61			0.320	4.447	15.22
	1	0.101	1.652	9.97	398.15	0	0.101	0.727	22.19			0.520	6.591	15.24
		0.295	5.561	9.96			0.520	4.329	22.22			1.021	12.33	15.30
		0.490	9.310	9.93			1.003	8.657	22.28			2.060	25.80	15.58
		0.736	14.71	9.95			2.000	16.49	22.40			2.926	38.25	15.81
		0.976	22.53	9.94			3.473	28.94	22.59			3.970	54.49	16.21
348.15	0	0.101	0.761	20.10			4.849	40.28	22.78			4.894	69.38	16.64
		0.518	5.043	20.16		0.246	0.101	0.853	19.17		1	0.101	1.009	13.32
		1.010	9.800	20.22			0.310	2.938	19.21			0.310	4.289	13.33
		2.028	19.63	20.37			0.519	5.150	19.19			0.505	6.812	13.35
	0.313	0.101	1.110	16.38			1.048	10.02	19.26			0.985	13.75	13.42
		0.294	3.552	16.39			2.030	19.75	19.43			2.022	30.21	13.70
		0.520	6.153	16.44			2.973	29.35	19.60			3.004	48.47	14.13
		0.998	11.96	16.50			3.839	37.95	19.74			4.015	71.30	14.77
		2.095	25.47	16.72			4.860	48.50	19.95			4.495	86.57	15.21
	0.491	0.101	1.237	14.63		0.525	0.101	0.885	16.17			4.912	99.15	15.68
		0.325	4.155	14.68			0.317	3.633	16.22					
		0.525	6.977	14.71			0.516	5.877	16.23					
		1.021	13.54	14.76			1.020	11.91	16.29					
		1.909	26.07	14.99			2.018	23.95	16.51					
	0.661	0.101	1.332	13.19			3.015	36.43	16.75					
		0.306	4.345	13.19			3.905	47.93	17.01					
		0.519	7.453	13.21			4.730	59.49	17.31					
		0.992	14.43	13.27		0.780	0.101	0.727	13.97					
		2.053	33.49	13.53			0.315	4.107	13.99					
	1	0.101	1.332	10.81			0.533	7.077	14.01					
		0.305	5.170	10.81			1.009	13.52	14.10					
		0.551	9.705	10.82			2.030	28.37	14.33					
		1.006	19.03	10.85			2.986	44.58	14.65					
		1.561	35.81	10.94			3.735	58.58	15.00					
		1.850	44.66	11.06			4.569	77.25	15.50					

$$\Omega^* = \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.77320T^*)} + \frac{2.16178}{\exp(2.43787T^*)} - 6.435 \cdot 10^{-4} T^{*0.14874} \sin(18.0323T^{*-0.7683} - 7.2731) \quad (2)$$

For methoxymethane, the Stockmayer potential was applied. Brokaw developed a simple approximation for Ω^* as follows[15]

$$\Omega^* = \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.77320T^*)} + \frac{2.16178}{\exp(2.43787T^*)} - 6.435 \cdot 10^{-4} T^{*0.14874} \sin(18.0323T^{*-0.7683} - 7.2731) + \frac{0.2\delta^2}{T^*} \quad (3)$$

The parameters for the Lennard−Jones potential and Stockmayer potential are listed in Table 2. The values of the parameters were determined from the gas viscosity data at 0.1 MPa.

For binary mixtures at 0.1 MPa, the viscosity η_m is expressed as follows:[16]

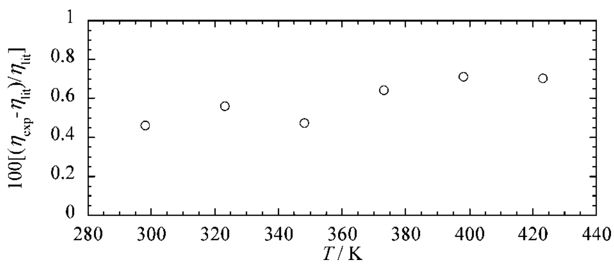

Figure 1. Deviations of the experimental viscosity data of nitrogen from the literature values.[13]

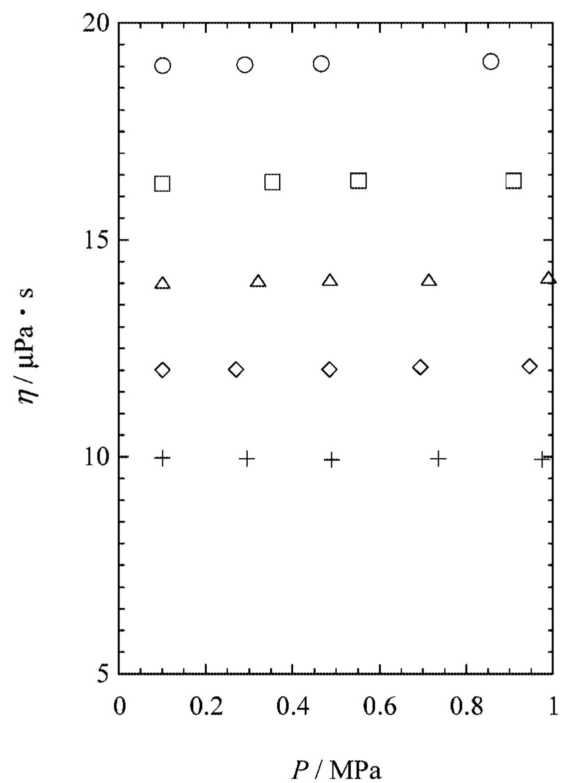

Figure 2. Viscosity of the methoxymethane + nitrogen mixtures at 323.15 K as a function of pressure. ○, $x_1 = 0$; □, $x_1 = 0.228$; Δ, $x_1 = 0.449$; ◊, $x_1 = 0.698$; +, $x_1 = 1$.

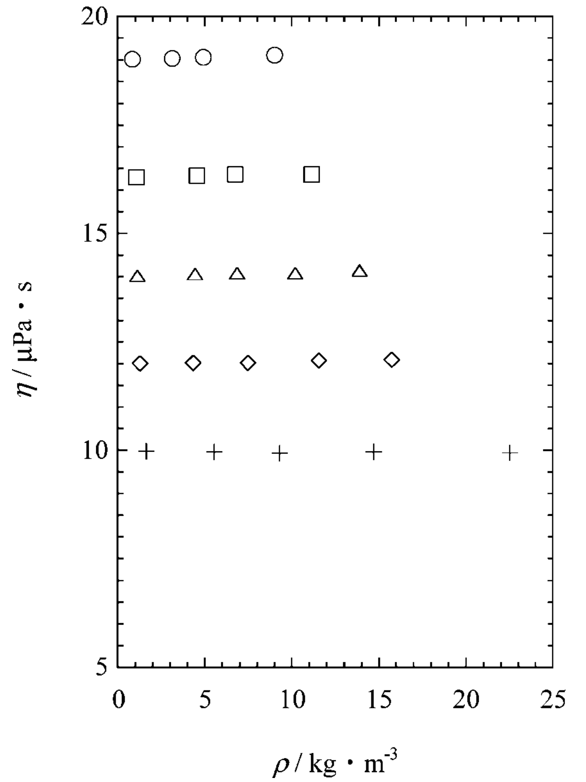

Figure 3. Viscosity of the methoxymethane + nitrogen mixtures at 323.15 K as a function of density. ○, $x_1 = 0$; □, $x_1 = 0.228$; Δ, $x_1 = 0.449$; ◊, $x_1 = 0.698$; +, $x_1 = 1$.

Table 2. Physical Properties and Potential Parameters for Methoxymethane and Nitrogen

	methoxymethane	nitrogen
molecular weight/g·mol^{-1}	46.069	28.013
T_c/K	400.00	126.20
ρ_c/(kg·m^{-3})	242	314
ε/k/(K)	467	105
σ/(10^{-10}m)	4.100	3.598
δ	0.17	

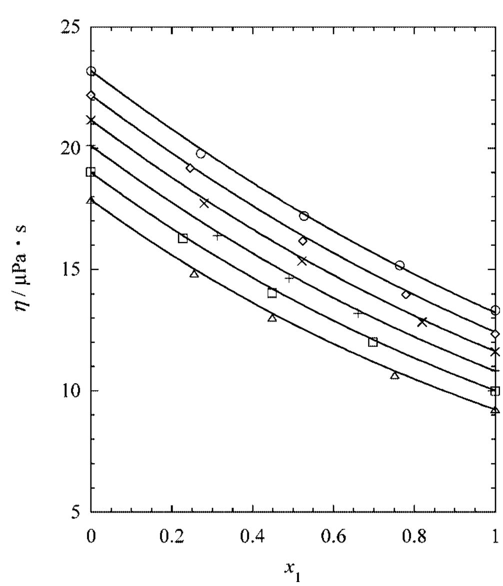

Figure 4. Viscosity of gaseous mixtures of the methoxymethane + nitrogen at 0.1 MPa. Δ, 298.15 K; □, 323.15 K; +, 348.15 K; ×, 373.15 K; ◊, 398.15 K; ○, 423.15 K; −, eq 4.

$$\eta_m/\mu\text{Pa}\cdot\text{s} = \frac{(1 + Z_\eta)}{(X_\eta + Y_\eta)} \quad (4)$$

$$X_\eta = \frac{x_1^2}{\eta_1^\circ/\mu\text{Pa}\cdot\text{s}} + \frac{2x_1x_2}{\eta_{12}^\circ} + \frac{x_2^2}{\eta_2^\circ/\mu\text{Pa}\cdot\text{s}} \quad (5)$$

$$Y_\eta = \frac{3A^*}{5}\left\{\frac{x_1^2}{\eta_1^\circ/\mu\text{Pa}\cdot\text{s}}\left(\frac{M_1}{M_2}\right) + \frac{2x_1x_2}{\eta_{12}^\circ}\left[\frac{(M_1+M_2)^2}{4M_1M_2}\right] \times \frac{(\eta_{12}^\circ)^2}{(\eta_1^\circ/\mu\text{Pa}\cdot\text{s})(\eta_2^\circ/\mu\text{Pa}\cdot\text{s})} + \frac{x_2^2}{\eta_2^\circ/\mu\text{Pa}\cdot\text{s}}\left(\frac{M_2}{M_1}\right)\right\} \quad (6)$$

$$Z_\eta = \frac{3A^*}{5}\left\{x_1^2\left(\frac{M_1}{M_2}\right) + 2x_1x_2\left[\frac{(M_1+M_2)^2}{4M_1M_2}\left(\frac{\eta_{12}^\circ}{\eta_1^\circ/\mu\text{Pa}\cdot\text{s}} + \frac{\eta_{12}^\circ}{\eta_2^\circ/\mu\text{Pa}\cdot\text{s}}\right) - 1\right] + x_2^2\left(\frac{M_2}{M_1}\right)\right\} \quad (7)$$

$$\eta_{12}^\circ = \frac{2.6695}{\sigma_{12}^2\Omega^*}\left(\frac{2M_1M_2T/\text{K}}{M_1+M_2}\right)^{1/2} \quad (8)$$

where η_i° is the viscosity of component i; x_i is mole fraction of component i; and subscripts 1 and 2 represent methoxymethane and nitrogen, respectively. A^* is a function of the reduced collision integral, and we correlated A^* in terms of the reduced temperature T^* in the range from 0.3 to 400.

$$A^* = 1.10192 - 7.7208\cdot10^{-3}\ln T^* - 1.17357\cdot10^{-2}(\ln T^*)^2 + 1.83419\cdot10^{-2}(\ln T^*)^3 - 7.08161\cdot10^{-3}(\ln T^*)^4 + 1.12192\cdot10^{-3}(\ln T^*)^5 - 6.40446\cdot10^{-5}(\ln T^*)^6 \quad (9)$$

For polar−nonpolar binary mixtures, the following mixing rule was applied

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)\xi^{-1/6} \quad (10)$$

$$\varepsilon_{12} = (\varepsilon_1\varepsilon_2)\xi^2 \quad (11)$$

$$\xi = 1 + \frac{1}{4}\alpha_2^*\mu_1^{*2}\left(\frac{\varepsilon_1}{\varepsilon_2}\right)^{1/2} \quad (12)$$

$$\alpha_2^* = \alpha_2\sigma_2^{-3} \quad (13)$$

$$\mu_1^* = \mu_1(\varepsilon_1\sigma_1^3)^{-1/2} \quad (14)$$

where α_2 is polarizability of nitrogen and μ_1 is dipole moment of methoxymethane. Those values are $1.76\cdot10^{-30}$ m^3 and 1.30 Debye, respectively.[16,17] For the binary mixture, Ω^* was calculated by eq 2, where $T^* = k(T/\text{K})/\varepsilon_{12}$ and k is the Boltzmann constant. Viscosity of the gaseous mixtures of methoxymethane + nitrogen at 0.1 MPa is shown in Figure 4. The solid lines in Figure 4 show the calculated results from the extended Chapman−Enskog equation. The deviations of the experimental viscosities from those calculated were 0.9 % on the average and 1.7 % at maximum.

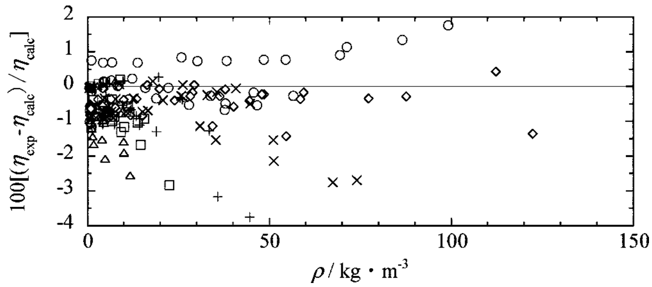

Figure 5. Deviations of the experimental data from eq 15. Δ, 298.15 K; □, 323.15 K; +, 348.15 K; ×, 373.15 K; ◊, 398.15 K; ○, 423.15 K.

Table 3. Parameters for Equation 15

a_1 (μPa·s)	a_2 (μPa·s)	a_3 (μPa·s)	a_4 (μPa·s)	a_5 (μPa·s)	a_6 (μPa·s)
1.0528	$4.6097\cdot10^{-2}$	$1.7892\cdot10$	$2.4041\cdot10^{-1}$	$-9.2398\cdot10$	$2.5000\cdot10^{2}$

The viscosity under pressures was expressed by the following empirical equation.

$$\eta/\mu\text{Pa}\cdot\text{s} - \eta^0/\mu\text{Pa}\cdot\text{s} = (a_1 + a_2T_r^3)\rho_{exr} + (a_3 + a_4T_r^3)\rho_{exr}^2 + (a_5/T_r)\rho_{exr}^4 + a_6\rho_{exr}^6 \quad (15)$$

where η and η^0 denote the viscosity at high pressures and at 0.1 MPa, respectively, and T_r and ρ_{exr} were reduced temperature and reduced density which are defined as follows

$$T_r = T/T_c \quad (16)$$

$$\rho_{exr} = (\rho - \rho_0)/\rho_c \quad (17)$$

where ρ and ρ_0 are the density at high pressure and at 0.1 MPa. The pseudocritical temperature of the mixture T_c and the pseudocritical density of the mixture ρ_c are defined as follows

$$T_c = x_1T_{c1} + x_2T_{c2} \quad (18)$$

$$\rho_c = x_1\rho_{c1} + x_2\rho_{c2} \quad (19)$$

The critical constants used in this study were quoted from the Thermophysical Properties Handbook[17] and were listed in Table 2. The values of constants a_i in eq 15 were determined with the use of a least-squares fitting and the experimental data. The values of constants are listed in Table 3. The deviations of experimental viscosity from this equation for the methoxymethane + nitrogen mixture were shown in Figure 5. It was found that this equation reproduced the experimental values with the maximum deviation of 3.8 % and the averaged deviation of 0.7 %.

4. Conclusion

The viscosities of a gaseous mixture of methoxymethane + nitrogen were measured with an oscillating-disk viscometer of the Maxwell type in the temperature range from (298.15 to 423.15) K and at pressures up to 4.97 MPa. The viscosity at 0.1 MPa was correlated with a maximum deviation of 1.7 %

and average deviation of 0.9 % by the Chapman−Enskog equation. For the viscosity at high pressure, the empirical equation reproduced the observed viscosity with a maximum deviation of 3.8 % and an averaged deviation of 0.7 %.

Literature Cited

(1) Wu, J.; Liu, Z.; Bi, S.; Meng, X. Viscosity of Saturated Liquid Methoxymethane from (227 to 343) K. *J. Chem. Eng. Data* **2003**, *48*, 426–429.

(2) Sivebaek, I. M.; Jakobsen, J. The viscosity of methoxymethane. *Tribol. Int.* **2007**, *40*, 652–658.

(3) Sivebaek, I. M.; Jakobsen, J. The viscosity of methoxymethane. *Tribol. Int.* **2008**, *41*, 839–843.

(4) Hongo, M.; Iwasaki, H. Viscosity of Nitrogen-Ammonia system under pressures. *Rev. Phys. Chem. Jpn.* **1977**, *47*, 90–101.

(5) Hongo, M.; Iwasaki, H. Viscosity of hydrogen and of hydrogen-ammonia mixtures under pressures. *Rev. Phys. Chem. Jpn.* **1978**, *48*, 1–9.

(6) Hongo, M. Viscosity of argon and of argon-ammonia mixtures under pressures. *Rev. Phys. Chem. Jpn.* **1978**, *48*, 63–71.

(7) Hongo, M. Initial Density dependence of viscosity of nonpolar polar gaseous-mixtures. *Rev. Phys. Chem. Jpn.* **1979**, *49*, 120–122.

(8) Hongo, M.; Yokoyama, C.; Takahashi, S. Viscosity of methane-chlorodifluoromethane (R22) gaseous mixtures in the temperature range from 298.15 to 373.15 K and at pressures up to 5 MPa. *J. Chem. Eng. Jpn.* **1988**, *21*, 632–639.

(9) Takahashi, M.; Yokoyama, C.; Takahashi, S. Viscosity of gaseous R13B1, R142b, and R152a. *J. Chem. Eng. Data* **1987**, *32*, 98–103.

(10) Takahashi, M.; Yokoyama, C.; Takahashi, S. Gas viscosity of non-azeotropic mixture of R22-R152a. *Trans. JAR.* **1987**, *4*, 25–36.

(11) Stephan, K.; Krauss, R.; Laesecke, A. Viscosity and Thermal Conductivity of Nitrogen for a Wide-Range of Fluid States. *J. Phys. Chem. Ref. Data* **1987**, *16*, 993–1023.

(12) Jacobsen, R. T.; Stewart, R. B. Thermodynamic properties of nitrogen including liquid and vapor phases from 63 to 2000. deg. K with pressures to 10,000 bar. *J. Phys. Chem. Ref. Data* **1973**, *2*, 757–922.

(13) Seibt, D.; Vogel, E.; Bich, E.; Buttig, D.; Hassel, E. Viscosity Measurements on Nitrogen. *J. Chem. Eng. Data* **2006**, *51*, 526–533.

(14) Neufeld, P. D.; Janzen, A. R.; Aziz, R. A. Empirical Equation to Calculate 16 of the Transport Collision Integrals $\Omega^{(l,s)*}$ for the Lennard-Jones (12-6) Potential. *J. Chem. Phys.* **1972**, *57*, 1100–1102.

(15) Brokaw, R. S. Predicting Transport Properties of Dilute Gases. *Ind. Eng. Chem. Process Des. Dev.* **1969**, *8*, 240–253.

(16) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Liquids and Gases*; Wiley: New York, 1954.

(17) Japan Society of Thermophysical Properties; *Thermophysical Properties Handbook*; Yokendo: Tokyo, 2008.

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