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

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The gas-phase viscosity of the methane-chlorodifluoromethane (R22) system was measured in the temperature range from 298.15 to 373.15 K and at pressures up to 5 MPa. The measurements were performed with a Maxwell type oscillating-disc viscometer. The viscosity at atmospheric pressure was correlated by three methods: the Chapman-Enskog equation, the Sutherland equation with Wilke combination factors and the Sutherland equation with Brokaw factors. It was found that the results calculated from the Sutherland equation with Brokaw combination factors gave the best agreement with the experimental data. The viscosity data at various pressures could not be correlated successfully by the residual viscosity correlations of Dean and Stiel or the equation of Pedersen *et al.* A new empirical equation for the correlation factor was proposed that extends the corresponding states viscosity equation with methane as the reference substance to the polar substance R22.

Introduction

Viscosity of gases, like thermal conductivity and diffusion coefficient, is an important physical 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.

Precise viscosity data of nonpolar gases over a wide range of temperature and pressure have received considerable attention. The viscosity of nonpolar gases increases with increasing pressure and/or density. This behavior can be expressed qualitatively by the Enskog theory⁶⁾ for dense gases. Few investigations of the viscosity of dense gas mixtures containing polar gases has been undertaken. Kestin and Wang²¹⁾ pointed out that the viscosity of water vapor decreases with an increase in pressure (and/or density) at a particular temperature and the anomalous behavior disappears as the temperature increases. This negative pressure (and/or density) effect on the viscosity was found experimentally for several polar gases, i.e., ammonia,^{5,11,17,34)} sulfur dioxide¹⁸⁾ and hydrocarbon fluorides,^{15,36-39)} and for gas mixtures

containing polar gases,^{11-13,16,40)} in addition to water vapor.^{20,21,27)} While it was found that an empirical correlating viscosity equation for pure gases can represent this negative pressure effect,^{15,19,33)} no equation has been proposed to express the effect of polar gases in gaseous mixtures. Therefore, it is interesting to develop an estimation method which can express the anomalous behavior of viscosity for nonpolar-polar gas mixtures.

In the present study the viscosities of methane-chlorodifluoromethane (R22) mixtures have been measured at 298.15, 323.15, 348.15 and 373.15 K up to 5 MPa by a Maxwell type oscillating-disc viscometer. The experimental viscosity values at atmospheric pressure were compared with calculated values from the Chapman and Enskog,¹⁰⁾ Wilke⁴¹⁾ and Brokaw^{3,4)} equations. The viscosities of the dense gas mixtures were calculated by two methods. One was the residual viscosity correlation of Dean and Stiel⁷⁾ with pseudocritical constants determined from the modified Prausnitz and Gunn rule.³¹⁾ The other was the corresponding states equation of Pedersen and Fredenslund.^{29,30)} We obtained a new empirical equation for a rotational coupling coefficient in order to extend the corresponding states equation to the polar gas R22.

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1. Experimental

The viscosities of methane and of methane-R22 gaseous mixtures were measured by a Maxwell type oscillating-disc viscometer. The apparatus and the experimental procedure were the same as those described in detail previously.^{11,12,15)} Measurements of viscosity were carried out at pressures up to 5 MPa and at temperatures of 298.15, 323.15, 348.15 and 373.15 K for methane, up to near the saturated vapor pressure of R22 from 298.15 to 348.15 K, and up to 5 MPa at 373.15 K for the mixtures. The density of gases required for the viscosity calculation was determined from the Benedict-Webb-Rubin equation of state.¹⁾ The eight constants in the BWR equation of state for pure gases were obtained from Benedict *et al.*¹⁾ for methane and from Nohka *et al.* for R22.²⁸⁾ The mixing rule of Benedict *et al.*²⁾ was used for the methane-R22 mixtures.

The methane used in this study was supplied from the Nihon Sanso Co., Ltd. and its purity was 99.95%. The R22 was supplied from the Daikin Kogyo Co., Ltd. and its purity was more than 99.0%. The R22 was purified by redistillation three times. The final purity of the R22 is estimated to be 99.9%. The composition of the mixture employed in this study was determined by use of gas chromatography. The experimental accuracy of the viscosity measurements is estimated to be within $\pm 0.3\%$.

2. Experimental Results

The experimental viscosity values for methane are given in **Table 1**. To ascertain the reliability of the present viscosity data, the viscosities of methane at atmospheric pressure and those at various other pressures are shown in **Figs. 1** and **2**, respectively, along with literature values by Hanley *et al.*⁹⁾ denoted by chain lines (the uncertainty: $\pm 2\%$) and by Makita *et al.*²³⁾ denoted by dashed lines (the uncertainty: $\pm 1.5\%$). As can be seen in Fig. 1, the viscosity values obtained in this study agree well with the two other evaluations, and in Fig. 2 the experimental viscosities are located between the two other evaluations at 298.15, 323.15 and 348.15 K, and are in agreement with those evaluations within the range of the respective uncertainties.

The viscosity values for the methane-R22 mixtures are summarized in **Table 2**. **Figure 3** shows the viscosity isotherms of the methane-R22 mixtures at atmospheric pressure. As shown in Fig. 3, the experimental viscosities vary non-linearly with composition and have a maximum at nearly 0.3 mol fraction of methane at each temperature.

Figure 4 represents the viscosity isotherms of methane-R22 mixtures at 298.15 K as a function of pressure. The viscosity values of pure R22 shown in

Table 1. Experimental viscosity values for methane

P [MPa]	ρ [kg/m ³]	η [μ Pa·s]	P [MPa]	ρ [kg/m ³]	η [μ Pa·s]
	298.15 K			348.15 K	
0.1013	0.6569	11.18	1.973	12.09	12.23
0.115	0.7425	11.19	3.519	21.98	12.51
0.170	1.105	11.19	4.724	29.93	12.75
0.292	1.898	11.19	0.1013	0.5620	12.79
0.498	3.248	11.23	0.523	2.914	12.83
1.021	6.730	11.30	1.542	8.675	12.94
1.506	10.01	11.33	2.596	14.75	13.10
2.029	13.61	11.41	3.580	20.52	13.27
2.522	17.06	11.53	4.739	27.43	13.45
3.001	20.48	11.59		373.15 K	
3.531	24.32	11.71	0.1013	0.5242	13.51
4.024	27.95	11.82	0.516	2.678	13.56
4.988	35.22	12.01	1.010	5.261	13.58
	323.15 K		2.030	10.65	13.72
0.1013	0.6056	11.98	2.937	15.50	13.84
0.524	3.150	12.03	4.086	21.72	14.00
0.972	5.878	12.08	4.943	26.40	14.14

Fig. 1. Experimental viscosity of methane at atmospheric pressure compared with literature values

Fig. 2. Experimental viscosity of methane at various pressures compared with literature values

Table 2. Experimental viscosity values for methane-R22 mixtures

298.15 K			323.15 K		
<i>P</i> [MPa]	ρ [kg/m ³]	η [μ Pa·s]	<i>P</i> [MPa]	ρ [kg/m ³]	η [μ Pa·s]
$x_{\text{CH}_4} = 0.240$			$x_{\text{CH}_4} = 0.237$		
0.1013	2.847	12.88	0.1013	2.652	13.92
0.283	8.179	12.86	0.341	9.106	13.94
0.499	14.79	12.83	0.742	20.52	13.98
0.710	21.63	12.87	1.238	35.95	14.00
1.002	31.73	12.91	1.718	52.61	14.26
$x_{\text{CH}_4} = 0.510$			$x_{\text{CH}_4} = 0.483$		
0.1013	2.080	12.86	0.1013	1.988	13.90
0.206	4.250	12.87	0.353	7.018	13.92
0.289	6.000	12.87	0.750	15.23	13.97
0.496	10.46	12.89	1.305	27.35	14.07
0.693	14.80	12.93	1.839	39.82	14.20
1.029	22.53	12.98	$x_{\text{CH}_4} = 0.748$		
$x_{\text{CH}_4} = 0.752$			0.1013	1.278	13.52
0.1013	1.375	12.43	0.354	4.496	13.56
0.200	2.718	12.46	0.763	9.803	13.57
0.296	4.043	12.47	1.310	17.10	13.68
0.500	6.878	12.50	1.863	24.72	13.78
0.699	9.699	12.50			
1.003	14.08	12.58			
348.15 K			373.15 K		
<i>P</i> [MPa]	ρ [kg/m ³]	η [μ Pa·s]	<i>P</i> [MPa]	ρ [kg/m ³]	η [μ Pa·s]
$x_{\text{CH}_4} = 0.290$			$x_{\text{CH}_4} = 0.268$		
0.1013	2.324	14.93	0.1013	2.217	15.94
0.357	8.312	14.97	0.531	11.86	16.01
0.858	20.59	15.04	1.514	35.50	16.24
1.539	38.61	15.20	2.533	62.84	16.64
2.149	56.33	15.44	3.525	92.96	17.31
2.770	76.29	15.84	4.489	126.68	18.19
$x_{\text{CH}_4} = 0.492$			$x_{\text{CH}_4} = 0.503$		
0.1013	1.820	14.88	0.1013	1.671	15.88
0.397	7.217	14.93	0.519	8.670	15.88
0.839	15.52	15.01	1.214	20.71	16.05
1.438	27.27	15.12	2.403	42.56	16.37
2.148	42.02	15.30	3.609	66.48	16.84
2.760	55.53	15.59	4.852	93.23	17.55
$x_{\text{CH}_4} = 0.777$			$x_{\text{CH}_4} = 0.750$		
0.1013	1.113	14.39	0.1013	1.100	15.39
0.337	3.720	14.40	0.528	5.776	15.40
0.768	8.551	14.44	1.505	16.72	15.55
1.466	16.55	14.57	2.518	28.44	15.75
2.200	25.20	14.69	3.519	40.38	16.04
3.080	35.91	14.88	4.510	52.55	16.35

this figure were reported previously.¹⁵⁾ Figure 4 shows the effect of composition on the isothermal behavior for this system; that is, a negative initial slope of the viscosity isotherm, $(\partial\eta/\partial P)_T$, for R22 changes sign as the concentration of methane increases. It is well known, however, that the gas viscosity can be expressed more easily as a function of density than as one of pressure.¹⁴⁾ Therefore, **Fig. 5** shows the relationship between viscosity and density rather than pressure at the same temperature. Variations in the

Fig. 3. Viscosity isotherm of methane-R22 mixtures at atmospheric pressure

Fig. 4. Viscosity of methane-R22 mixtures at 298.15 K as a function of pressure

Fig. 5. Viscosity of methane-R22 mixtures at 298.15 K as a function of density

initial slope of the isotherm observed at constant composition can be seen more clearly than those shown in Fig. 4. The same behavior can be seen for the case of the 323.15 K isotherm, and similar behavior has been reported in the nitrogen–ammonia,¹¹⁾ hydrogen–ammonia,¹²⁾ and argon–ammonia^{13,16)} systems.

3. Correlation of Gas Viscosity

3.1 Viscosity at atmospheric pressure

1) Chapman–Enskog Equation The viscosity of low-density gas mixtures can be estimated by both theoretical and empirical equations. The equation of viscosity for a binary gas mixture was derived by Chapman and Enskog on the basis of rigorous kinetic theory, and is expressed as follows:⁸⁾

$$\eta_m^\circ = \left(\frac{x_1^2}{H_{11}^\circ} + \frac{x_2^2}{H_{22}^\circ} - \frac{2x_1x_2H_{12}^\circ}{H_{11}^\circ H_{22}^\circ} \right) / \left(1 - \frac{(H_{12}^\circ)^2}{H_{11}^\circ H_{22}^\circ} \right) \quad (1)$$

where x_i is the mole fraction of component i , and

$$H_{12}^\circ = -\frac{2x_1x_2}{\eta_{12}^\circ} \frac{M_1M_2}{(M_1+M_2)^2} \left(\frac{5}{3A^*} - 1 \right) \quad (2)$$

$$H_{11}^\circ = \frac{x_1^2}{\eta_{11}^\circ} + \frac{2x_1x_2}{\eta_{12}^\circ} \frac{M_1M_2}{(M_1+M_2)^2} \left(\frac{5}{3A^*} + \frac{M_2}{M_1} \right) \quad (3)$$

The expression for H_{22}° is obtained from that for H_{11}° by interchanging the species subscripts 1 and 2. The η_{12}° is the low-density viscosity of a hypothetical pure gas whose molecular mass is $2M_1M_2/(M_1+M_2)$ and whose molecular interaction is according to the real 1–2 interaction. The A^* is a dimensionless ratio of collision integrals and is given by Hirschfelder *et al.*¹⁰⁾ and Monchick *et al.*^{25,26)}

The η_{12}° is expressed as follows.

$$\eta_{12}^\circ = 2.6695 \times 10^{-6} \frac{\sqrt{2M_1M_2T/(M_1+M_2)}}{\sigma_{12}^2 \Omega_\eta(T_{12}^*)} \quad (4)$$

where M_1 is a molecular mass of component 1, $T_{12}^* = kT/\epsilon_{12}$ is reduced temperature, σ_{12} and ϵ_{12} are parameters in the potential function characteristic of 1–2 interaction, and k is a Boltzmann constant. When the subscript 2 is replaced by 1, Eq. (4) expresses the gas viscosity of pure component 1, η_{11}° . We used the Lennard–Jones potential for methane–methane interaction, and the Stockmayer potential for R22–R22 interaction.

The Lennard–Jones potential was used for the methane–R22 interaction, whose potential parameters were expressed by the following combining rule.¹⁰⁾

$$\epsilon_{12} = \chi^2 (\epsilon_{11} \epsilon_{22})^{1/2} \quad (5)$$

$$\sigma_{12} = (1/2) \chi^{-1/6} (\sigma_{11} + \sigma_{22}) \quad (6)$$

in which

Table 3. Potential parameters used in the present study

	σ [10^{-10} m]	ϵ/k [K]	δ [—]
CH ₄	3.692	163	
CHClF ₂ *	4.711	261	0.28

* cf. ref. 15.

$$\chi = 1 + (1/2) \alpha_1^* \delta_2 (\epsilon_{22}/\epsilon_{11})^{1/2} \quad (7)$$

where $\alpha_1^* = \alpha_1/\sigma_1^3$ is a reduced polarizability of methane and $\delta_2 = \mu_2^2/2\epsilon_2\sigma_2^3$ is the reduced dipole moment of R22. The potential parameters for methane and R22 were determined by fitting the calculated values from Eq. (4) to the experimental data at atmospheric pressure. The potential parameters are listed in **Table 3**. The calculated results are shown in Fig. 3 by solid lines.

2) Sutherland Equation While various empirical equations for viscosity calculation of gas mixtures have been presented, the most successful was given by Sutherland as follows.³⁵⁾

$$\eta_m^\circ = \frac{\eta_{11}^\circ}{1 + \phi_{12}(x_2/x_1)} + \frac{\eta_{22}^\circ}{1 + \phi_{21}(x_1/x_2)} \quad (8)$$

where ϕ_{12} and ϕ_{21} are the combination factors.

Wilke⁴¹⁾ proposed an approximation formula for ϕ_{12} and ϕ_{21} by using Sutherland's kinetic theory. The ϕ_{12} and ϕ_{21} are expressed as follows.

$$\phi_{12} = \frac{[1 + (\eta_{11}^\circ/\eta_{22}^\circ)^{1/2} (M_2/M_1)^{1/4}]^2}{[8(1 + M_1/M_2)]^{1/2}} \quad (9)$$

$$\phi_{21} = (\eta_{22}^\circ/\eta_{11}^\circ) (M_1/M_2) \phi_{12} \quad (10)$$

Brokaw^{3,4)} obtained the following equations for a gas mixture containing polar gas by making an approximation to the rigorous kinetic theory.

$$\phi_{ij} = (\eta_{ii}^\circ/\eta_{jj}^\circ)^{1/2} S_{ij} F_{ij} \quad (11)$$

where

$$F_{ij} = m_{ij} M_{ij}^{-1/2} \left[1 + \frac{M_{ij} - M_{ij}^{0.45}}{2(1 + M_{ij}) + \frac{(1 + M_{ij}^{0.45})}{(1 + m_{ij})} m_{ij}^{-1/2}} \right] \quad (12)$$

with

$$m_{ij} = \left[\frac{4}{(1 + M_{ij}^{-1})(1 + M_{ij})} \right]^{0.25} \quad (13)$$

$$M_{ij} = M_i/M_j \quad (14)$$

If the polarity parameter δ is greater than 0.1 for either component i or j , S_{ij} is defined as

$$S_{ij} = S_{ji} = \frac{1 + (T_i^* T_j^*)^{1/2} + (\delta_i \delta_j / 4)}{[1 + T_i^* + (\delta_i^2 / 4)]^{1/2} [1 + T_j^* + (\delta_j^2 / 4)]^{1/2}} \quad (15)$$

Table 4. Deviation between experimental and calculated viscosity at atmospheric pressure for CH₄-R22 system

Temp. [K]	Deviation [%]*								
	Chapman-Enskog (Eqs. (1)-(4))			Wilke (Eqs. (8)-(10))			Brokaw (Eqs. (8) & (11))		
	Ave.	Bias	Max.	Ave.	Bias	Max.	Ave.	Bias	Max.
298.15	0.34	0.34	0.55	0.76	-0.76	1.35	0.16	0.10	0.31
323.15	0.64	0.60	1.35	0.67	-0.67	0.79	0.44	0.30	0.97
348.15	0.75	0.70	1.70	0.61	-0.61	0.80	0.53	0.45	1.27
373.15	0.80	0.72	1.58	0.50	-0.50	0.56	0.65	0.61	1.38
Total	0.63	0.59	1.70	0.64	-0.64	1.35	0.45	0.36	1.38

* Deviation

$$\text{Ave.} = 100 \sum \{(\eta_{\text{exp}}^{\circ} - \eta_{\text{cal}}^{\circ}) / \eta_{\text{cal}}^{\circ}\} / n$$

$$\text{Bias} = 100 \sum \{(\eta_{\text{exp}}^{\circ} - \eta_{\text{cal}}^{\circ}) / \eta_{\text{cal}}^{\circ}\} / n$$

$$\text{Max.} = \text{maximum of } 100 \{|\eta_{\text{exp}}^{\circ} - \eta_{\text{cal}}^{\circ}| / \eta_{\text{cal}}^{\circ}\}$$

n = number of data

where $T_i^* = kT/\varepsilon_i$. If δ values of both components are less than 0.1, $S_{ij} = S_{ji} = 1$.

The calculated results from the Wilke equation and the Brokaw equation are shown in Fig. 3 by dashed lines and dot-dash lines, respectively. The deviations between the experimental data and the calculated values are listed in **Table 4**. It can be seen from Fig. 3 and Table 4 that all three methods give a maximum near 0.3 mole fraction of methane and that Brokaw's equation indicates the best reproducibility.

3.2 Viscosity of gas mixtures under pressure

The theoretical equations for dense-gas viscosity were derived on the basis of the kinetic theory and the corresponding states principle. The empirical equation for dense-gas mixture viscosity was developed by Thodos and coworkers.^{7,19,33} Dean and Stiel⁷ proposed an empirical viscosity equation for dense-gas mixture as follows.

$$(\eta_m - \eta_m^{\circ})\xi_m = 0.108[\exp(1.439\rho_{rm}) - \exp(-1.11\rho_{rm}^{1.858})] \quad (16)$$

where η_m is dense-gas mixture viscosity, η_m° is dilute-gas mixture viscosity, $\rho_{rm} = \rho_m/\rho_{cm}$ is pseudoreduced mixture density, ρ_m is mixture density, $\rho_{cm} = P_{cm}/(Z_{cm} \cdot R \cdot T_{cm})$ is pseudocritical mixture density and $\xi_m = T_{cm}^{(1/6)}/M_m^{(1/2)}P_{cm}^{(2/3)}$ is a viscosity parameter. The mixture molecular weight M_m is a mole fraction average defined by Eq. (22). The pseudocritical mixture parameters, Z_{cm} , T_{cm} and P_{cm} , were calculated from the modified Prausnitz and Gunn mixing rule.³¹⁾

$$\begin{aligned} T_{cm} &= \sum_i x_i T_{ci} \\ Z_{cm} &= \sum_i x_i Z_{ci} \\ V_{cm} &= \sum_i x_i V_{ci} \\ P_{cm} &= Z_{cm} \cdot R \cdot T_{cm} / V_{cm} \end{aligned} \quad (17)$$

Table 5. Deviation between experimental data and calculated values from Eq. (16)

Substance	Deviation [%]*		
	Ave.	Bias	Max.
CH ₄	0.37	-0.37	1.31
R22	3.34	-3.34	6.97
Mixture	1.21	-1.21	3.75

* Deviation

$$\text{Ave.} = 100 \sum \{(\eta_{\text{exp}} - \eta_{\text{cal}}) / \eta_{\text{cal}}\} / n$$

$$\text{Bias} = 100 \sum \{(\eta_{\text{exp}} - \eta_{\text{cal}}) / \eta_{\text{cal}}\} / n$$

$$\text{Max.} = \text{maximum of } 100 \{|\eta_{\text{exp}} - \eta_{\text{cal}}| / \eta_{\text{cal}}\}$$

n = number of data

The deviation between the experimental data and the calculated values from Eq. (16) is listed in **Table 5**. It should be noted that the Dean and Stiel equation cannot represent the viscosity decrease of polar gases with increasing density at low temperature.

Pedersen *et al.*^{29,30)} presented a new method for predicting oil and gas mixtures based on the corresponding states principle. The viscosity of a gas mixture at a given pressure P and temperature T is given as follows.

$$\eta_m = \left(\frac{T_{CM}}{T_{C0}}\right)^{-1/6} \left(\frac{P_{CM}}{P_{C0}}\right)^{2/3} \left(\frac{M_M}{M_0}\right)^{1/2} \frac{\alpha_m}{\alpha_0} \times \eta_0 \left[\frac{P \cdot P_{C0} \cdot \alpha_0}{P_{CM} \cdot \alpha_m}, \frac{T \cdot T_{C0} \cdot \alpha_0}{T_{CM} \cdot \alpha_m} \right] \quad (18)$$

where

$$\begin{aligned} T_{CM} &= \sum_i \sum_j x_i x_j \left[\left(\frac{T_{Ci}}{P_{Ci}}\right)^{1/3} + \left(\frac{T_{Cj}}{P_{Cj}}\right)^{1/3} \right]^3 (1 - k_{ij}) [T_{Ci} T_{Cj}]^{1/2} \\ &= \frac{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{Ci}}{P_{Ci}}\right)^{1/3} + \left(\frac{T_{Cj}}{P_{Cj}}\right)^{1/3} \right]^3}{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{Ci}}{P_{Ci}}\right)^{1/3} + \left(\frac{T_{Cj}}{P_{Cj}}\right)^{1/3} \right]^3} \end{aligned} \quad (19)$$

$$P_{CM} = \frac{8 \sum_i \sum_j x_i x_j \left[\left(\frac{T_{Ci}}{P_{Ci}} \right)^{1/3} + \left(\frac{T_{Cj}}{P_{Cj}} \right)^{1/3} \right]^3 (1 - k_{ij}) [T_{Ci} T_{Cj}]^{1/2}}{\left\{ \sum_i \sum_j x_i x_j \left[\left(\frac{T_{Ci}}{P_{Ci}} \right)^{1/3} + \left(\frac{T_{Cj}}{P_{Cj}} \right)^{1/3} \right]^3 \right\}^2} \quad (20)$$

$$M_M = M_m + 0.291(\overline{M_m} - M_m) \quad (21)$$

$$M_m = \sum_i x_i M_i \quad (22)$$

$$\overline{M_m} = \frac{\sum_i x_i M_i^2}{\sum_i x_i M_i} \quad (23)$$

$$\alpha_m = 1 + 7.747 \times 10^{-5} \rho_r^{4.265} M_M^{0.8579} \quad (24)$$

$$\alpha_0 = 1 + 8.374 \times 10^{-4} \rho_r^{4.265} \quad (25)$$

where k_{ij} in Eqs. (19) and (20) is a binary interaction parameter. The reduced density ρ_r is calculated from

$$\rho_r = \frac{\rho_0 \left(\frac{T \cdot T_{C0}}{T_{CM}}, \frac{P \cdot P_{C0}}{P_{CM}} \right)}{\rho_{C0}} \quad (26)$$

The subscript 0 indicates the reference substance. The reference substance is methane and the viscosity equation of methane is quoted from Hanley *et al.*⁽⁹⁾ and the equation of state from McCarty.⁽²⁴⁾ The calculated results from Pedersen's equation are listed in Table 6. As can be seen, the error of this equation is comparable to that of the Dean and Stiel equation. The calculated viscosity of R22 from Eq. (18) deviates from the experimental data by about 10%. One of the reasons for this discrepancy may be that the rotational coupling coefficients, Eqs. (24) and (25), are not successful. Pedersen *et al.*⁽²⁹⁾ determined Eqs. (24) and (25) by using viscosity data of hydrocarbons. The α_0 and α_m correspond to the shape factor of the corresponding states principle proposed by Leach *et al.*⁽²²⁾ Sarashina *et al.*⁽³²⁾ extended the corresponding states principle to systems containing a polar substance. The shape factor determined from the PVT data of ammonia was a rather complicated equation of temperature and density. In this study, we determined the following equation for the ratio of the coupling factors, α_m/α_0 , by using the viscosity data for R22

$$\alpha_m/\alpha_0 = x_1 + x_2 \cdot J_M \quad (27)$$

$$J_M = a_0 + a_1/T_r + (a_2 + a_3/T_r)\rho_r \quad (28)$$

where subscript 1 of x is methane and subscript 2 is R22 in Eq. (27), and $T_r = T/T_{CM}$, $\rho_r = \rho/(P_{CM}/(R \cdot T_{CM}))$ in Eq. (28). Constants a_0 – a_3 in Eq. (28) are as follows:

$$a_0 = 1.00835 \quad a_1 = -0.37370$$

$$a_2 = 1.50727 \quad a_3 = -1.42618$$

Table 6. Comparison between experimental data and calculated values from Pedersen's original equation and by use of new correlation factor

		Deviation [%]*		
		Ave.	Bias	Max.
Original method (Eqs. (18) with (24) & (25))	CH ₄	0.46	−0.43	1.88
	R22	7.37	−7.37	10.23
	Mixture	8.86	−8.86	11.27
This work (Eqs. (18) with (27))	CH ₄	0.45	−0.42	1.83
	R22	1.04	−0.48	2.93
	Mixture ($k_{ij}=0$)	6.97	−6.97	11.43
	Mixture ($k_{ij} = -0.460$)	0.88	0.08	3.71

* Definition of deviation is the same as in Table 5.

The results of Eq. (27) are also shown in Table 6, and illustrated in Figs. 4 and 5 by solid lines. It was found that the correlation with the experimental data for the methane–R22 mixtures was improved remarkably by the use of k_{ij} as a fitting parameter.

Conclusion

To investigate the viscosity of a nonpolar–polar gas mixture under pressure, we measured the viscosity of the methane–R22 system in the temperature range from 298.15 to 373.15 K and at pressures up to 5 MPa.

The viscosity decreased as pressure or density increased in the pressure range from 0.1013 to 0.499 MPa and at 298.15 K and $x_{CH_4} = 0.240$. The same behavior has been observed for some polar gases. Sutherland's equation with Brokaw's combination factor gave the best results for viscosity of the gas mixtures at atmospheric pressure. The residual viscosity correlation of Dean and Stiel with the Gunn and Prausnitz mixing rule was first applied to calculate the viscosity at various pressures. The deviation between experimental and calculated values was typically between −3.4 to 7.0%. The corresponding states correlation of Pedersen *et al.* was found to give practically the same results for the residual viscosity correlation. We proposed a new empirical correlation factor for a corresponding states correlation that gives improved results for R22. Using the new correlation factor, it was found that the corresponding states correlation could predict the viscosity of methane–R22 system within 3.7% de-

viation from the experimental data.

Nomenclature

A^*	= collision integral ratio = Ω_{η}/Ω_D	[—]
$a_0 \sim a_3$	= constants in Eq. (28)	
F_{ij}	= function of molecular weight defined in Eq. (12)	
J_M	= function defined in Eq. (28)	
k	= Boltzman constant (1.380622×10^{-23})	[J/K]
k_{ij}	= binary interaction parameter	[—]
M	= molecular weight	
M_{ij}	= molecular weight ratio defined in Eq. (14)	[—]
M_M	= mixture molecular weight defined in Eq. (21)	
M_m	= weight average molecular weight	
m_{ij}	= function of molecular weight defined in Eq. (13)	[—]
P	= pressure	[Pa]
P_{CM}	= critical mixture pressure defined in Eq. (20)	
R	= gas constant (8.31441)	[m ³ ·Pa/(K·mol)]
$S_{ij} = S_{ji}$	= function of polarity parameter in Eqs. (11) and (15)	[—]
T	= temperature	[K]
T_{CM}	= critical mixture temperature defined in Eq. (19)	[—]
T_i^*	= reduced temperature = kT/ε_i	[—]
V	= molar volume	[m ³ /mol]
x	= mole fraction	[—]
Z	= compressibility factor	[—]
α	= polarizability	[m ³]
α_0	= coupling factor of reference substance	[—]
α_m	= coupling factor of mixture	[—]
δ	= polarity parameter = $\mu^2/(2\varepsilon\sigma^3)$	[—]
ε	= potential parameter	[J]
η	= gas viscosity	[Pa·s]
η_{12}^o	= hypothetical gas viscosity defined in Eq. (4)	[Pa·s]
μ	= dipole moment	[C·m]
ξ_m	= viscosity parameter of gas mixture	[—]
ρ	= density	[kg/m ³]
ρ_r	= reduced density defined in Eq. (26)	[—]
σ	= potential parameter	[m]
ϕ	= combination factor	[—]
χ	= constant defined in Eq. (7)	[—]
Ω	= reduced collision integral	[—]

<Subscripts>

1, 2, i, j	= molecule 1, 2, i and j
c	= critical property
cal	= calculated
cm	= pseudocritical property
D	= diffusion
exp	= experimental
m	= mixture property
r	= property reduced by critical constant
rm	= pseudoreduced mixture property
η	= viscosity
0	= reference substance

<Superscripts>

*	= property reduced by potential parameter
o	= dilute gas property

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FLOW STRUCTURE AND MIXING MECHANISM IN AN AGITATED THIN-FILM EVAPORATOR

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Key Words: Fluid Mechanics, Agitation, Evaporator, Thin-Film Flow, Mixing

The flow structure and mixing mechanism of the high-viscosity fluid in an agitated thin-film evaporator were experimentally and numerically investigated. Film thickness, holdup and power consumption were measured, and velocity distributions were numerically calculated using a finite element method. The results show that most of the fluid flows down in a fillet and that mixing between fillet and film is extremely suppressed. This also suggests that usual thin-film evaporators are not always effective.

Introduction

Agitated thin-film evaporators are widely used to concentrate polymer solutions by evaporating solvents in industrial processes. The evaporator can be operated in a vacuum, and the residence time of a solution in the equipment can be reduced to less than a few seconds. The agitated thin-film evaporator can therefore find wide application in food, pharmaceutical and petrochemical processes which involve the operations of refining, concentration or deodorization. In such processes the solutions are often prone to thermal decomposition, or have the high viscosity or low thermal conductivity, making the thin-film evaporator even more useful. The evaporator equipment and its application are described in detail by Leonald³⁾ and Mutzenburg *et al.*⁵⁾

An agitated thin-film evaporator with a rotor blade is sketched in Fig. 1. The supplied fluid flows down along the vertical cylindrical shell-wall and is agitated by a rotor blade. A clearance is held as a gap between the fixed blade-tip and the cylindrical wall. The agitation by the blade forms a film falling along the cylindrical wall and a falling fillet in the periphery of the blade. The falling film consists of both a radial drag flow due to the rotor blade and a downward flow due to gravity. The fillet consists of a falling spiral flow. These flow configurations suggest that the film flow may contribute both to heat transfer between the

fluid and the cylindrical wall and evaporation through the film surface, and that the fillet flow may predominate in momentum and mass transfer between the film and the fillet. Thus, it is of great importance to investigate the flow structure and mixing mechanism in the film and fillet flows in designing an effective thin-film evaporator.

Kern and Karakas²⁾ and Godau¹⁾ analytically calculated the film thickness and falling velocity of high-viscosity fluid in the thin-film evaporator under isothermal conditions without evaporation. Their analyses were based on the equations of motion. However, they neither compared the predictions with the measurements nor analyzed the flow structure in the fillet. Nakamura and Watanabe⁶⁾ investigated the low-viscosity flow in an agitated thin-film evaporator under isothermal operating conditions. They approximately estimated the fillet size on the (r, θ) -plane and calculated the liquid holdup by means of a

Fig. 1. Schematic diagram of an agitated thin-film evaporator and flow field