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VISCOSITY OF PROPYLENE UNDER PRESSURES

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The viscosity of propylene was measured by use of an oscillating disk viscometer in the pressure range below the saturated vapor pressure of propylene at 25, 50 and 75°C, up to about 43×10^5 Pa at 100°C, and up to about 56×10^5 Pa at 125°C. The accuracy of the measurements was estimated to be within ±0.5 %. An initial decrease in viscosity in the low density region could not be observed.

The initial density dependence of viscosity, $\alpha' = \eta_0^{-1}(\partial\eta/\partial\rho)_{\rho\to 0}$, of propylene was determined from the experimental values and compared with the calculated α'-values, where η is viscosity; ρ density; and η_0 the viscosity extrapolated to zero density. α' increased with a decrease in a polarity parameter, δ, and with a rise in temperature in the correlation between α' and a polarity for six polar gases.

Introduction

The transport coefficients of gases, i.e., viscosity, thermal conductivity, and diffusion coefficient, are important physical properties in order to know molecular interactions. The precise measured values of these transport properties under pressures are useful to solve theoretically the molecular motion in dense gaseous state and to obtain the method of accurate prediction of the properties.

It is well known[1] that gas viscosity depends upon pressure or density. The viscosity of nonpolar gases increases with an increase in pressure or density, while the viscosity of polar gases below a certain temperature decreases with an increase in pressure or density, and after its negative slope gradually approaches zero, the viscosity increases with an increase in pressure or density in the higher temperature range as well as that of nonpolar gases[2~5]. However, there are only a few investigations about the viscosity, which shows the peculiar behavior, of polar gases under pressures.

In this paper, propylene whose dipole moment is 0.364 Debye was taken as an example of a polar gas. The viscosities of gaseous propylene under pressures were measured by Golubev *et al.*, by Neduzhiy *et al.* and by Naziev *et al.*[6], but it was insufficient to investigate the initial slope of the viscosity isotherm by applying the experimental data. So, the viscosities of propylene were measured by

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[1] T. Makita, "Viscosity and Thermal Conductivity", Baifukan, Tokyo (1975)

[2] M. Hongo and H. Iwasaki, *This Journal*, **47**, 90 (1977)

[3] H. Iwasaki and M. Takahashi, *Bull. Chem. Soc. Japan*, **48**, 988 (1975)

[4] A. Nagashima, I. Tanishita and Y. Murai, *J. Chem. Eng. Data*, **19**, 212 (1974)

[5] H. Iwasaki and M. Takahashi, *This Journal*, **38**, 18 (1968)

[6] Y. Tanaka and T. Makita, *ibid.*, **45**, 93 (1975)

use of a precision oscillating disk-type viscometer at pressures below the saturated vapor pressure of propylene from 25 to 75°C, up to about 43×10^5 Pa at 100°C, and up to about 56×10^5 Pa at 125°C.

Experimental

Measurements of the viscosity were carried out by means of an oscillating disk viscometer, which was the same as that described in early papers[2,5,7]. The apparatus constant C_N' was obtained from the calibration measurements made by using nitrogen whose viscosity was precisely determined.

The calculating method of the gas viscosity is the same as that mentioned previously[2]. The density of propylene required for the calculation was obtained through the compressibility factors recommended by Date *et al.*[8] Commercial propylene was supplied from the Takachiho Kagakukogyo K. K., and its purity was above 99.7%. Propylene was purified by redistillation three times.

The accuracy of the experimental viscosity values was estimated to be within ±0.5%.

Results

The experimental viscosity values of gaseous propylene are presented in Table 1 and plotted in Fig. 1 as a function of pressure. The viscosity isotherm of polar gases, such as ammonia[2,5], sulfur

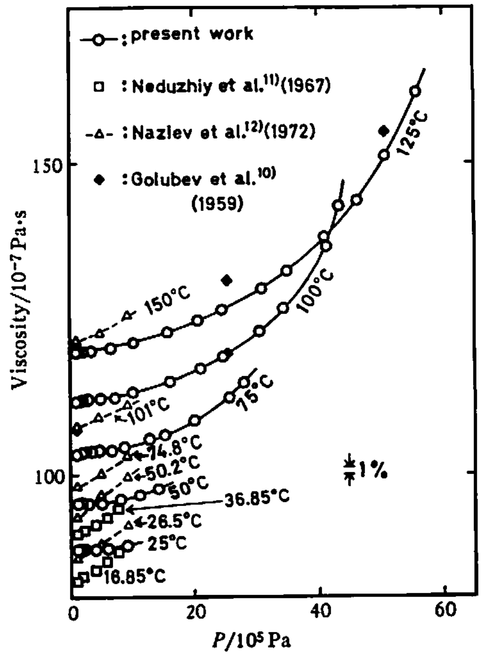

Fig. 1 The viscosity of propylene as a function of pressure: ○ present work (25, 50, 75, 100 and 125°C), □ Neduzhiy *et al.* (16.85 and 36.85°C), △ Naziev *et al.* (26.5, 50.2, 74.8, 101 and 150°C), ◆ Golubev *et al.*(100 and 150°C)

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7) M. Hongo and H. Iwasaki, *This Journal*, **48**, 1 (1978)
8) K. Date and H. Iwasaki, *ibid.*, **44**, 1 (1974)

Table 1 Viscosity of propylene

Pressure 10^5 Pa	Density 10^3kg·m^{-3}	Viscosity 10^{-7}Pa·s	Pressure 10^5 Pa	Density 10^3kg·m^{-3}	Viscosity 10^{-7}Pa·s
	25℃			100℃	
1.27	0.00219	87.8	1.04	0.00141	111.6
1.55	0.00269	87.8	1.30	0.00164	111.7
2.03	0.00354	87.8	1.53	0.00210	111.6
4.10	0.00740	87.9	2.05	0.00282	111.7
6.09	0.0114	88.0	2.94	0.00407	112.0
9.16	0.0183	88.5	4.91	0.00690	112.1
			7.40	0.0106	112.3
	50℃		10.27	0.01505	113.1
			16.22	0.02506	114.9
1.27	0.00201	95.4	21.19	0.03442	116.9
1.50	0.00239	95.2	24.89	0.04213	118.9
2.03	0.00324	95.4	30.55	0.05564	122.9
3.04	0.00492	95.4	34.45	0.06670	126.5
5.07	0.00841	95.4	41.44	0.09188	136.6
8.11	0.0140	96.0	43.45	0.1015	143.1
11.15	0.02024	96.6			
14.30	0.02753	97.9		125℃	
	75℃		1.03	0.00131	119.6
			1.23	0.00157	119.6
1.01	0.00147	103.4	1.54	0.00198	119.6
1.36	0.00200	103.3	2.10	0.00270	119.7
1.67	0.00247	103.6	3.54	0.00459	119.9
2.00	0.00296	103.6	6.59	0.00870	120.3
2.48	0.00369	103.6	10.29	0.01392	121.2
3.45	0.00516	103.8	15.76	0.02211	122.8
4.90	0.00745	104.0	20.67	0.03003	124.8
6.70	0.0104	104.0	24.55	0.03677	126.5
8.82	0.0139	104.5	31.02	0.04908	129.9
12.89	0.02001	105.7	35.01	0.05747	132.6
15.44	0.02639	106.4	41.05	0.07180	138.1
20.16	0.03686	108.6	46.25	0.08609	144.0
25.66	0.05195	112.3	50.80	0.1006	151.1
28.03	0.06002	114.6	55.95	0.1195	161.3

dioxide[3)] and water vapor[4,9)] shows a steady decrease with increasing pressure in the lower temperature region and shows a steady increase with increasing pressure above a certain temperature. However, as can be seen from Table 1 and Fig. 1, an initial decrease in viscosity cannot be observed in the case of propylene. Above the critical temperature (T_c=92°C), as the pressure coefficient of viscosity, $(\partial\eta/\partial P)_T$, at 125°C is smaller than that at 100°C, two viscosity isotherms cross each other, where η is viscosity; P pressure; and T temperature.

The gas viscosities of propylene under pressures were measured by Golubev[10)] (18 to 250°C, 1 to 800 atm), by Neduzhiy *et al.*[11)] (210 to 310 K, 0.98 to 7.84 bar) and by Naziev *et al.*[12)] (26.5 to 200.6°C,

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9) J. Kestin and H. E. Wang, *Physica*, **26**, 575 (1960)

10) I. F. Golubev, "Viscosity of Gases and Gaseous Mixtures" Moscow, Fizmatgiz (1959) (Israel Program for Scientific Translations (1970))

11) D. M. Vashchenko *et al.*, "Thermodynamic and Transport Properties of Ethylene and Propylene" (Translated from the Russian as published by the State Committee of Standards of the Soviet Ministry, U. S. S. R.), N. B. S., U. S. Dept. of Commerce, Washington, D. C. (1972)

12) Ya. M. Naziev, S. O. Gusejnov and A. K. Akhmedov, *Izv. Vyssh. Ucheb. Zaved., Neft Gaz.*, **15**(6), 65 (1972)

1.01 to 9.2 bar). These measurements were made using a capillary-flow viscometer. The data reported by the above-mentioned investigators are also shown in Fig. 1. The viscosity values obtained by Neduzhiy *et al.* and Naziev *et al.* increase more rapidly with pressure than those obtained in this work.

Figure 2 shows the relation between the experimental viscosity and density. As shown in the figure, each isotherm is almost parallel to one another, and it is found that the initial slopes of the isotherms, $(\partial\eta/\partial\rho)_{\rho\to 0}$, where ρ is density, are nearly zero or positive in the experimental conditions.

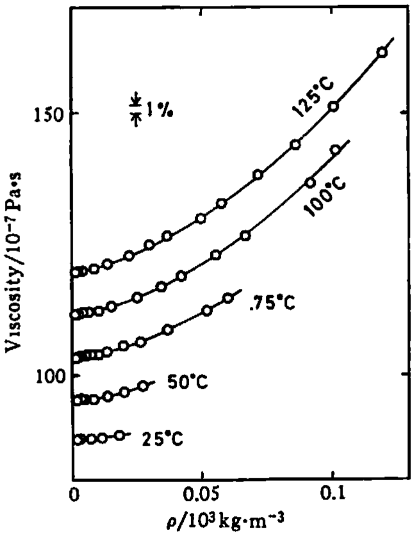

Fig. 2 The viscosity of propylene as a function of density

The viscosity values of propylene at atmospheric pressure were obtained by the extrapolation of the viscosity vs. pressure curves to 1 atm (1.013×10^5 Pa), and are shown in Fig. 3 in comparison

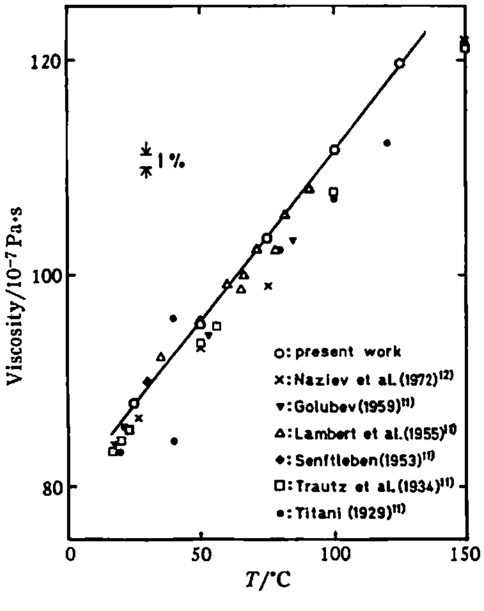

Fig. 3 The viscosity of propylene at atmospheric pressure

with six investigations, *i. e.*, Titani[11] (20 to 120°C), Trautz *et al.*[11] (16.75 to 248.55°C), Senftleben[11] (30°C), Lambert *et al.*[11] (35 to 90.8°C), Golubev[11] (18 to 250°C) and Naziev *et al.*[12] (26.5 to 200.6°C). Among the available viscosity data, the values obtained by Senftleben and by Lambert *et al.* agree well with those obtained in this work, but the difference between the values obtained by Trautz *et al.*, by Golubev and by Naziev *et al.* and those obtained in this work becomes larger as temperature increases and it shows about 4% at 125°C.

Discussion

As seen from Fig. 2, it is considered that the gas viscosity is easier to be expressed as a function of density than pressure[13]. So, the gas viscosity isotherm can be approximately expressed as follows:

$$\eta=\eta_0(1+\alpha'\rho+\cdot\cdot\cdot\cdot\cdot) \tag{1}$$

where η_0 is the viscosity extrapolated to zero density and $\alpha'=\eta_0^{-1}(\partial\eta/\partial\rho)_{\rho\to0}$ is the initial density dependence of viscosity[2]. In order to study α' of propylene, the coefficients of several kinds of polynomials were calculated by applying the experimental viscosity values. As described in the previous paper[14], it was found that the lower order equation could better reproduce the low density region rather than the higher order equation. Therefore, the data which had only some measured points in the low density region was expressed by linear or quadratic equation, and the other was expressed by cubic equation. The coefficients of polynomials obtained are shown in Table 2.

Table 2 Coefficients of $\eta=\eta_0(1+\alpha'\rho+\beta'\rho^2+\gamma'\rho^3)$ (η in 10^{-7} Pa·s; ρ in 10^3 kg·m^{-3})

T/℃	n_i	η_0	α'	β'	γ'	stand. dev.
25	6	87.6	0.475			0.102
50	8	95.3	−0.143	40.6		0.089
75	14	103.3	0.558	24.4	−56.6	0.131
100	15	111.4	0.952	12.6	52.1	0.327
125	16	119.4	0.952	17.8	− 9.21	0.105

On the other hand, the theoretically calculated α'-values of a polar gas were obtained from the following equation[14]

$$\frac{M\alpha'}{b_0}=-B_{\mathrm{d}}^{\star}(T)\left[0.5113+0.2481\left(\frac{6D_{\mathrm{dm}}}{D_{\mathrm{mm}}}-4.5455\frac{D_{\mathrm{mm}}}{D_{\mathrm{dm}}}\right)\right]\cdot\frac{10}{(T^*)^{2.3}}\log(1+\sqrt[3]{\delta})$$
$$+0.1750\left[B^{\star}(T)+T^*\left(\frac{\mathrm{d}B^{\star}}{\mathrm{d}T^*}\right)\right]\cdot\frac{10}{(T^*)^{1.5}} \tag{2}$$

where $B^{\star}=B/b_0=(B_{\mathrm{f}}+B_{\mathrm{b}}+B_{\mathrm{m}})/b_0$; $B_{\mathrm{d}}^{\star}=(B_{\mathrm{b}}+B_{\mathrm{m}})/b_0$; $b_0=2\pi N\sigma^3/3$; B: second virial coefficient; B_{f}: the contribution attributed to collisions between free molecules; B_{b} and B_{m}: the contribution from

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13) T. Makita, *High Pressure Gas*, **11**, 582 (1974)

14) M. Hongo, *This Journal*, **49**, 1 (1979)

the equilibrium constant for the formation of bound double molecules and metastable double molecules, respectively; D: diffusion coefficient; the subscripts dm and mm denote dimer-monomer and monomer-monomer interactions; M: molecular weight; $T=T^*/\varepsilon k^{-1}$; N: Avogadro's number; k: the Boltzman constant; T: absolute temperature; and σ, ε and δ: potential parameters.

Eq. (2) was obtained[14] by the improvement of the original theoretical equation (Eq. (10) in Ref. 14) which was derived by Stogryn *et al.*[15] The calculating method was detailed in the previous paper[14]. It was necessary to know the potential parameters of propylene before the calculation. The parameters for the modified Stockmayer potential function[1] used in this study were determined from the same way as described previously[7,16] and by use of the experimental viscosity values at atmospheric pressure. The rerult of the determination was as follows:

$$C_3H_6:\quad \sigma=4.27_1\,[\text{Å}],\qquad \varepsilon/k=399\,[\text{K}],\qquad \delta=0.02$$

Figure 4 shows the comparison of the experimental and calculated values of $M\alpha'/b_0$ of propylene.

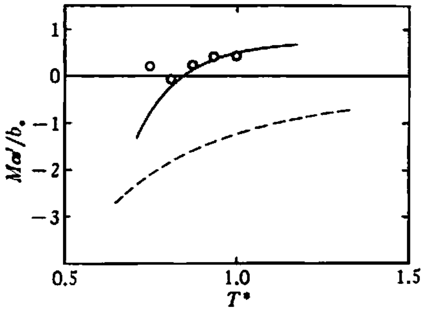

Fig. 4 A comparison of the experimental and calculated values of $M\alpha'/b_0$ for propylene

As shown in the figure, the calculated values obtained from the right hand side of Eq. (2) (denoted by a solid line) are in better agreement with the experimental ones (by the symbol ○) than the original theoretical ones (by a dashed line).

In order to investigate the relation between the initial density dependence of viscosity and a polarity, the experimental α'-values were correlated to $\log(1+\sqrt[6]{\delta})$ which represented the corrected term of Eq. (2) with the polarity parameter, δ. Figure 5 shows the correlation between α' and

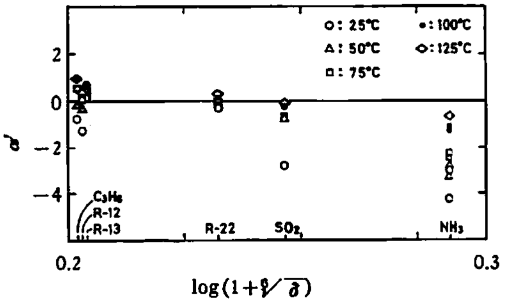

Fig. 5 The correlation between α' and $\log(1+\sqrt[6]{\delta})$ for six polar gases

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15) D. E. Stogryn and J. O. Hirschfelder, *J. Chem. Phys.*, **31**, 1545 (1959)

16) M. Hongo, *This Journal*, **48**, 63 (1978)

$\log(1+\sqrt[6]{\delta})$ for propylene together with ammonia[14], sulfur dioxide[14], and three hydrocarbon halides[14], that is, CCl_2F_2 (R-12), $CClF_3$ (R-13) and $CHClF_2$ (R-22). As can be seen from the figure, α' increases with a decrease in δ and with a rise in temperature. Accordingly it may be adequately conceivable that a clear initial decrease in viscosity cannot be observed in the low pressure or density region in Figs. 1 and 2.

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