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VISCOSITY OF HYDROGEN AND OF HYDROGEN-AMMONIA MIXTURES UNDER PRESSURES*

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The viscosity of gaseous hydrogen and of gaseous hydrogen-ammonia mixtures of four different ratios was measured using an oscillating disk-type viscometer at temperatures of 25, 50, 75, and 100°C, and in the pressure range up to about 120×10^5 Pa for hydrogen and up to the vicinity of the saturated vapor pressure of ammonia for hydrogen-ammonia mixtures. The accuracy of the measurements is estimated to be within ±0.3%.

In the calculation of the gas viscosity of dilute binary mixtures based on Chapman-Enskog's theory, a modification of the combination rule using the critical compressibility factor was presented. The calculated viscosity values obtained by applying the critical compressibility factor were in better agreement with the experimental ones than the original Chapman-Enskog's theoretical ones.

The initial density dependence of the viscosity of hydrogen-ammonia mixtures, *i. e.*, $\eta_0^{-1}(\partial\eta/\partial\rho)_{\rho\to0}$, increased with an increase in temperature and in the mole fraction of hydrogen as in the case of the nitrogen-ammonia system, where η is the viscosity of a gas, η_0 is the viscosity extrapolated to zero density, and ρ is density. Further, it may be concluded that the nonpolar molecules of larger molecular weight disturb more strongly the dimerization of polar molecules than those of smaller molecular weight.

Introduction

Among the transport coefficients of a gas, on consideration of the molecular theory of gases the viscosity is an important physical property because it can be measured very precisely. The accurate experimental values of the viscosity of gaseous mixtures under various pressures are useful to obtain some information about intermolecular interactions and contribute to the theoretical development for dense gaseous mixtures. In recent years accurate measurements of the gas viscosity at high pressure or at high temperature have been made, but the studies about the viscosity of gaseous mixtures under pressures are not so many. Especially, as mentioned in the previous paper[1], there are only a few investigations[1,2,3] about the viscosity of nonpolar-polar mixtures under pressures. Therefore, as the example of the nonpolar-polar system, the viscosity of hydrogen-ammonia mixtures has been measured using a precision oscillating disk-type viscometer following the nitrogen-ammonia system[1]. In order to study the effect of the molecular weight of nonpolar gas on the viscosity of

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

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polar gas, hydrogen was selected because its molecular weight is the smallest among nonpolar gases.

Measurements of the viscosity have been carried out at temperatures, 25, 50, 75 and 100°C and at pressures up to about 120×10^5 Pa for hydrogen and up to around the saturated vapor pressure of ammonia for hydrogen-ammonia mixtures, *i. e.*, about 10×10^5 Pa at 25°C, 20×10^5 Pa at 50°C, 35×10^5 Pa at 75°C and 60×10^5 Pa at 100°C. The viscosity of the hydrogen-ammonia system at atmospheric pressure was measured by Trautz *et al.*4) (20 to 250°C) using a capillary-flow viscometer and by Pal *et al.*5) (33 to 206°C) using an oscillating disk viscometer, but there are no other viscosity data of this system to be compared with above atmospheric pressure.

Experimental Method

The apparatus and the experimental procedure are much the same as those reported in detail previously1). But thermister thermometers were used instead of thermocouples to measure the temperatures of the pressure vessel and the oil in the thermostat. These thermister thermometers were calibrated against a platinum resistance thermometer provided with a calibration certificate by the National Bureau of Standards. The accuracies of the temperature measurements were ±0.01°C from 25 to 75°C and ±0.02°C at 100°C.

Hydrogen was supplied from the Nippon Oxygen Co., Ltd. and its purity was 99.99%. Ammonia was purified as described previously1).

Calculation of Viscosity

The viscosity of the gases has been calculated in the same way as described in Ref. 2. The apparatus constant, C_N', was determined using nitrogen at the temperature of 25°C and at pressures below 25×10^5 Pa. The mean value of C_N' used in the present calculation was 1.1337 for hydrogen from 25 to 75°C, and 1.1355 for hydrogen at 100°C and for hydrogen-ammonia mixtures from 25 to 100°C.

The densities required for the calculation were obtained from the *PV* values reported by Michels *et al.*6) for hydrogen and from *V*ri chart prepared by K. Tezuka7) for hydrogen-ammonia mixtures, where *V*ri is the ideal reduced molar volume. The accuracy of the experimental values of viscosity was estimated to be within ±0.3%.

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4) M. Trautz and R. Heberling, *Ann. Physik*, **10**, 155 (1931)
5) A. K. Pal and A. K. Barua, *J. Chem. Phys.*, **47**, 216 (1967)
6) A. Michels and M. Goudeket, *Physica*, **8**, 347 (1941)
7) K. Satoh, "Bussei Josu Suisanho", Maruzen, Japan (1954)

Results

The experimental results obtained for hydrogen are given in Table 1 and plotted in Fig. 1. The viscosity of hydrogen at the same experimental conditions as those of this work were already measured by Michels *et al.*[8] (25 to 75°C), Barua *et al.*[9] (25 to 75°C), and Gracki *et al.*[10] (25°C). They are also shown in Fig. 1. The values obtained in this work agree well with those obtained in the investigations described above within the experimental error. The experimental data given in Table 1 show that the initial slopes of the viscosity *vs.* pressure curves are slightly negative at 25, 50 and 75°C, although this behavior cannot be seen clearly in Fig. 1. Similar observations were pointed out by Chuang *et al.*[11] and others[9,10], but the decrement ratio was smaller than the experimental accuracy.

The viscosity values obtained for hydrogen-ammonia mixtures are shown in Table 2. For example, the results obtained for mixtures at 25°C are shown in Fig. 2. The viscosity values for pure ammonia have already been reported in Ref. 1. It is apparent that the initial slope of the viscosity *vs.* pressure curves of each mixture, *i. e.*, $(\partial\eta/\partial P)_{P\to0}$, increases as the mole fraction of hydrogen increases, where η is the viscosity of gases and P is the pressure. Fig. 3 shows the isobaric

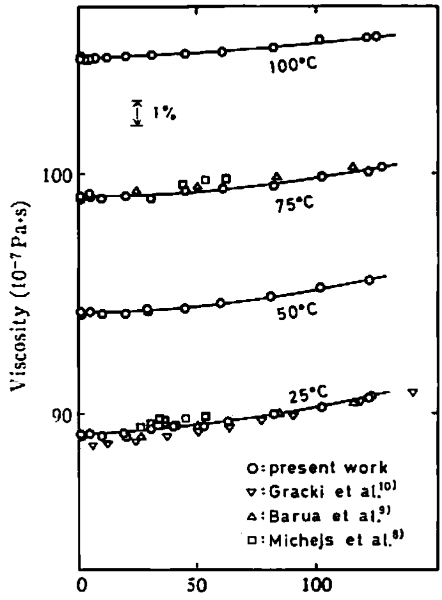

Fig. 1 Viscosity of hydrogen

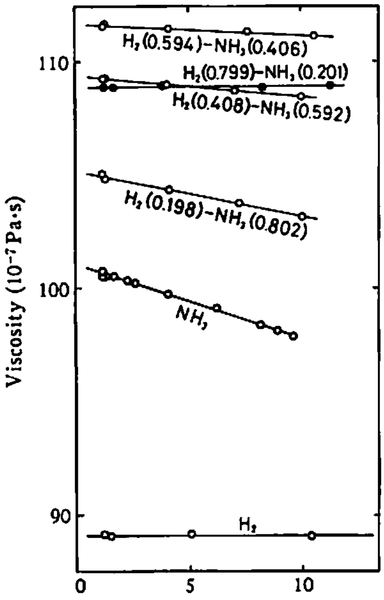

Fig. 2 Viscosity of hydrogen-ammonia system at 25°C

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8) A. Michels, A. C. J. Schipper and W. H. Rintoul, *Physica*, **19**, 1011 (1953)
9) A. K. Barua, M. Afzal, G. P. Flynn and J. Ross, *J. Chem. Phys.*, **41**, 374 (1964)
10) J. A. Gracki, G. P. Flynn and J. Ross, *J. Chem. Phys.*, **51**, 3856 (1969)
11) S. Chuang, P. S. Chappelear and R. Kobayashi, *J. Chem. Eng. Data*, **21**, 403 (1976)

Table 1 Viscosity of hydrogen

Pressure 10^5 Pa	Density 10^3 kg·m^{-3}	Viscosity 10^{-7} Pa·s	Pressure 10^5 Pa	Density 10^3 kg·m^{-3}	Viscosity 10^{-7} Pa·s
	25°C			75°C	
1.22	0.0000983	89.1	1.19	0.0000821	99.0
1.51	0.000122	89.1	1.26	0.0000870	99.0
5.09	0.000411	89.2	5.07	0.000351	99.0
10.42	0.0008422	89.1	5.09	0.000352	99.1
19.77	0.001590	89.2	10.13	0.0007014	99.0
20.39	0.001640	89.0	20.24	0.001398	99.0
31.09	0.002481	89.3	31.25	0.002140	99.0
40.56	0.003223	89.5	45.72	0.003110	99.3
41.42	0.003290	89.5	61.24	0.004131	99.4
53.11	0.004190	89.5	82.75	0.005521	99.5
63.52	0.004979	89.7	102.55	0.006773	99.8
82.56	0.006398	89.9	122.20	0.007989	100.0
102.80	0.007875	90.2	127.63	0.008321	100.2
122.16	0.009254	90.7			
122.99	0.009312	90.7		100°C	
			1.22	0.0000785	104.8
	50°C		1.26	0.0000811	104.8
1.19	0.0000884	94.1	2.03	0.000131	104.8
1.34	0.0000998	94.3	3.05	0.000197	104.8
5.12	0.000382	94.3	5.08	0.000328	104.8
10.30	0.0007686	94.2	7.11	0.000459	104.8
20.29	0.001506	94.2	12.17	0.0007859	104.8
29.74	0.002195	94.4	20.32	0.001308	104.9
45.27	0.003315	94.4	31.39	0.002010	105.0
60.33	0.004380	94.6	45.58	0.002896	105.0
81.19	0.005826	94.9	61.06	0.003849	105.1
101.98	0.007230	95.2	82.29	0.005133	105.3
122.48	0.008597	95.5	101.79	0.006290	105.6
122.50	0.008598	95.5	121.29	0.007431	105.7
			125.31	0.007662	105.7

behavior of the viscosity of the hydrogen-ammonia system at 100°C. These curves show that the influence of pressure on the viscosity is not so large below the saturated vapor pressure of ammonia at the experimental conditions. All isobars obtained in the present measurements have the maximum at about 0.6 mole fraction of hydrogen.

The viscosity values of mixtures at atmospheric pressure were obtained by extrapolating the viscosity *vs.* pressure curves to 1 atm (1.013×10^5 Pa), and are shown in Fig. 4 along with the data reported by Trautz *et al.*4) (20 and 100°C) and by Pal *et al.*5) (33, 54 and 98°C). The values obtained by Trautz *et al.*4) agree with those obtained in this work within ±1% at 100°C. However, the values obtained by Pal *et al.*5) are fairly different from those obtained in this work, although the experimental temperatures are not the same.

Table 2 Viscosity of hydrogen-ammonia mixtures

Pressure 10^5 Pa	Density 10^3 kg·m^{-3}	Viscosity 10^{-7} Pa·s	Pressure 10^5 Pa	Density 10^3 kg·m^{-3}	Viscosity 10^{-7} Pa·s	Pressure 10^5 Pa	Density 10^3 kg·m^{-3}	Viscosity 10^{-7} Pa·s
	25°C			50°C			100°C	
	H_2 (0.198)–NH_3 (0.802)			H_2 (0.794)–NH_3 (0.206)			H_2 (0.202)–NH_3 (0.798)	
1.22	0.000689	104.9	1.23	0.000233	116.4	1.26	0.000567	133.0
1.30	0.000735	104.7	1.34	0.000254	116.4	1.62	0.000731	133.0
4.15	0.00236	104.2	5.09	0.000967	116.3	5.12	0.00231	132.8
7.28	0.00428	103.6	10.12	0.001919	116.3	10.14	0.004625	132.6
10.06	0.006154	103.0	15.25	0.002894	116.2	20.35	0.009700	132.4
			20.25	0.003867	116.2	30.55	0.01509	132.5
	H_2 (0.408)–NH_3 (0.592)		25.23	0.004809	116.4	40.80	0.02065	132.8
1.24	0.000544	109.1				50.82	0.02665	133.4
1.34	0.000588	109.1		75°C		60.89	0.03300	134.3
4.07	0.00179	108.8		H_2 (0.201)–NH_3 (0.799)		62.21	0.03385	134.5
7.09	0.00317	108.6	1.27	0.000613	122.8			
10.03	0.004518	108.3	1.54	0.000746	122.6		H_2 (0.404)–NH_3 (0.596)	
			5.13	0.00248	122.4	1.28	0.000451	136.3
	H_2 (0.594)–NH_3 (0.406)		10.16	0.005109	122.0	1.55	0.000548	136.4
1.22	0.000398	111.4	15.22	0.007811	121.7	5.16	0.00182	136.2
1.31	0.000428	111.5	25.26	0.01346	121.2	10.23	0.003675	136.1
4.15	0.00136	111.3	35.53	0.01961	121.0	20.28	0.007390	135.9
7.65	0.00252	111.2	38.34	0.02132	121.0	30.65	0.01131	136.2
10.63	0.003520	111.0				40.82	0.01542	136.1
				H_2 (0.398)–NH_3 (0.602)		50.63	0.01946	136.4
	H_2 (0.799)–NH_3 (0.201)		1.26	0.000480	126.3	60.45	0.02354	137.2
1.26	0.000255	108.8	1.52	0.000580	126.4	63.89	0.02498	137.4
1.62	0.000337	108.7	5.08	0.00194	126.1			
3.84	0.000780	108.7	10.13	0.003945	125.9		H_2 (0.594)–NH_3 (0.406)	
8.28	0.00169	108.7	15.20	0.006005	125.8	1.22	0.000318	137.6
11.34	0.002338	108.8	25.27	0.01014	125.5	1.27	0.000331	137.5
			35.82	0.01447	125.4	5.12	0.00134	137.5
	50°C		39.23	0.01591	125.5	10.11	0.002635	137.7
	H_2 (0.189)–NH_3 (0.811)					20.28	0.005300	137.6
1.22	0.000642	113.3		H_2 (0.599)–NH_3 (0.401)		30.77	0.008085	137.6
1.34	0.000707	113.4	1.22	0.000338	127.9	40.75	0.01081	137.6
5.05	0.00267	112.9	1.52	0.000422	127.9	50.88	0.01358	137.9
10.15	0.005580	112.2	5.07	0.00141	127.8	60.98	0.01636	138.2
15.23	0.008620	111.6	10.11	0.002867	127.6	66.47	0.01780	138.5
20.35	0.01189	111.0	15.13	0.004257	127.6	66.48	0.01781	138.3
24.14	0.01427	110.3	25.25	0.007050	127.7			
			35.58	0.01005	127.7		H_2 (0.800)–NH_3 (0.200)	
	H_2 (0.400)–NH_3 (0.600)		39.99	0.01140	127.8	1.22	0.000197	131.7
1.23	0.000503	117.4				1.31	0.000211	131.9
1.26	0.000516	117.5		H_2 (0.802)–NH_3 (0.198)		5.13	0.000830	131.9
5.07	0.00208	117.0	1.21	0.000208	123.1	10.24	0.001680	131.9
12.69	0.005358	116.5	1.34	0.000231	122.9	20.29	0.003358	131.9
20.34	0.008758	116.2	5.07	0.000874	123.1	31.62	0.005155	132.2
24.06	0.01040	115.9	10.13	0.001750	123.2	41.09	0.006615	132.1
			15.22	0.002629	123.2	51.60	0.008240	132.4
	H_2 (0.600)–NH_3 (0.400)		25.29	0.004331	123.0	61.60	0.009750	132.6
1.24	0.000369	119.7	35.66	0.006135	123.3	64.57	0.01019	132.7
1.49	0.000441	119.6	40.77	0.007079	123.3	64.58	0.01020	132.8
5.07	0.00151	119.6						
12.69	0.003887	119.4						
20.27	0.006226	119.2						
24.23	0.007431	119.1						

Discussion

Modification of the combination rule for the nonpolar-polar system

The viscosity of dilute gaseous binary mixtures can be evaluated by the method based on the kinetic theory[12]. The theoretical equation to the first approximation derived by Chapman and Enskog

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[12] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids", John Wiley & Sons, Inc., New York (1954)

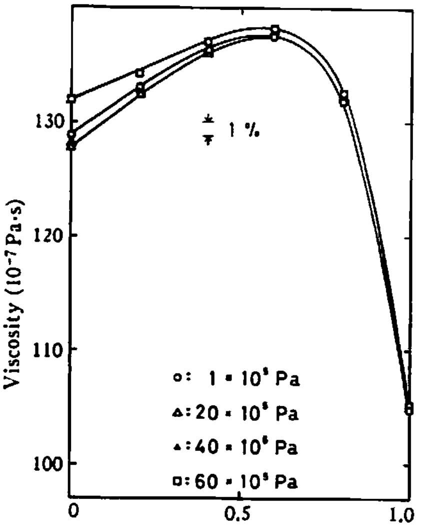

Fig. 3 Viscosity isobar of hydrogen-ammonia system at 100°C

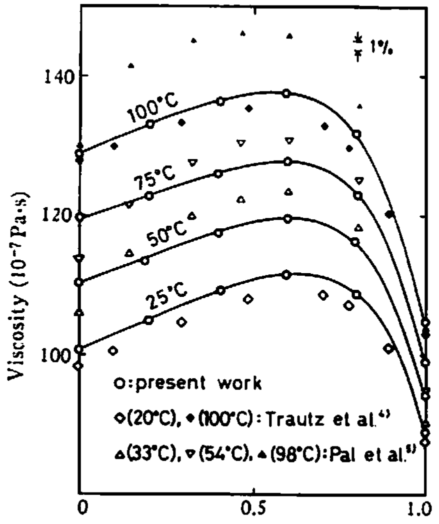

Fig. 4 Viscosity of hydrogen-ammonia system at atmospheric pressure

is expressed by Eq. (8.2-22) in Ref. 12. In the calculation using the above equation, it is necessary to know the force constants between unlike molecules. The combination rules for nonpolar-polar interactions are represented as follows:

$$\sigma_{np}=\frac{1}{2}(\sigma_n+\sigma_p)\xi^{-1/6} \qquad (1)$$

$$\varepsilon_{np}=(\varepsilon_n\varepsilon_p)^{1/2}\xi^{2} \qquad (2)$$

where σ_n and ε_n are the Lennard-Jones potential parameters for the nonpolar molecules, σ_p and ε_p are the Stockmayer potential parameters for the polar molecules, and ξ is defined in Eq. (8.6-5) in Ref. 12. These parameters for pure gases in Eqs. (1) and (2) were calculated from Eq. (8.2-19) through third approximation in Ref. 12 for hydrogen and from Eq. (8.2-18) in Ref. 12 for ammonia[1] using the experimental viscosity values of the gases at atmospheric pressure. The mean values are given as follows:

$$H_2: \quad \sigma_n=2.93_2\,[\text{Å}], \quad \varepsilon_n/k=38.0\,[\text{K}]$$

$$NH_3: \quad \sigma_p=3.15_8\,[\text{Å}], \quad \varepsilon_p/k=358\,[\text{K}], \quad \delta=0.7$$

For the calculation of $[\eta_{mix}]_1$ based on Eq. (8.2-22) in Ref. 12, the theoretical viscosity values of hydrogen $[\eta_1]_1$ were determined from Eq. (8.2-19) ($k=3$) by use of its potential parameters presented above and those of ammonia $[\eta_2]_1$ were similarly done from Eq. (8.2-18) at each temperature.

Fig. 5 shows the comparison of the theoretical values based on Chapman-Enskog's theory (dashed line) with the experimental values (solid line). It may be seen from this figure that the experimental values obtained in this work are higher than the theoretical ones, and that the difference increases in the hydrogen-rich region as temperature rises up and it becomes about 3% at

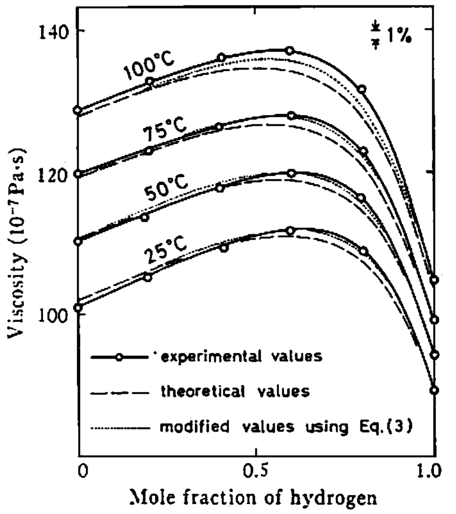

Fig. 5 Comparison of experimental value with original theoretical one and calculated one applying Eq. (3) in hydrogen-ammonia system

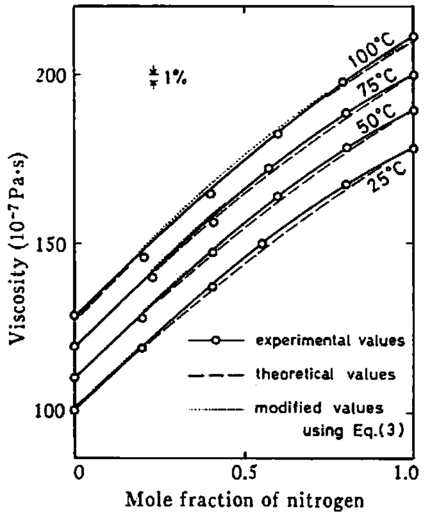

Fig. 6 Comparison of experimental value with original theoretical one and calculated one applying Eq. (3) in nitrogen-ammonia system

100°C.

In this study, it has been tried to modify the combination rule, Eqs. (1) and (2), using critical constants to fit to the experimental viscosity values, since there were some empirical methods[13,14] to obtain the potential parameter by use of critical constants. It was found that the calculated values agreed well with the experimental values, when ε_{np} was somewhat decreased. So, the critical compressibility factor, Z_c, was adopted to set up a correction factor, as it was known[15] that a modification using Z_c expressed satisfactory results. Z_c of most substances have nearly constant values 0.24~0.31. The following equation was chosen, as a result of testing various formulae using Z_c.

$$\left(\frac{\varepsilon_{np}}{k}\right)' = \frac{\varepsilon_{np}}{k}\left\{(Z_{cn})^{1/2}+(Z_{cp})^{1/2}\right\}^{-2} \qquad (3)$$

where Z_{cn} and Z_{cp} are critical compressibility factors of nonpolar and polar substances, respectively. The viscosity values of $[\eta_{mix}]_1$ obtained by applying Eq. (3), shown by dotted lines in Fig. 5, are in good agreement with the experimental ones.

The above-described method was also applied to the nitrogen-ammonia system[1], and the results are shown in Fig. 6. The force constants used for the nitrogen-ammonia system were obtained as follows:

N_2: $\sigma_n=3.73_2$ [Å], $\varepsilon_n/k=79.8$ [K]

As can be seen from Figs. 5 and 6, the viscosity values obtained by using Eq. (3) agree very closely with the experimental ones from 25 to 75°C, but do not agree sufficiently at 100°C.

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13) E. A. Halkiadakis and R. G. Bowrey, *Chem. Eng. Sci.*, **30**, 53 (1975)
14) L. I. Stiel and G. Thodos, *AIChE Journal*, **10**, 266 (1964)
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Initial density dependence of the viscosity for the nonpolar-polar system

The gas viscosity η can be approximately expressed as a function of the density ρ as follows:

$$\eta=\eta_0(1+\alpha'\rho+\cdots\cdots\cdots) \qquad (4)$$

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[1]. In this work the experimental viscosities of hydrogen and hydrogen-ammonia mixtures were expressed by the cubic equation as

$$\eta=\eta_0(1+\alpha'\rho+\beta'\rho^2+\gamma'\rho^3) \qquad (5)$$

and the constants in Eq. (5) were determined by means of the least-squares method as given in Table 3. The relation between α' and x_{H_2} at each temperature is shown in Fig. 7, where α' denotes the initial density dependence of the viscosities of ammonia[1] and of hydrogen-ammonia mixtures, and x_{H_2}, the mole fraction of hydrogen. As shown in the figure, each isotherm is approximated by a straight line, and then it is found in the nitrogen-ammonia system[1] that α' increases with an increase in temperature and in the mole fraction of hydrogen and that $x_{H_2}^\circ$, the mole fraction of hydrogen at a point of intersection of each straight line with $\alpha'=0$, decreases with an increase in temperature. Fig. 8 shows that there is the linear relation between $x_{H_2}^\circ$ and temperature. It should be noted that the similar relation was observed in case of the nitrogen-ammonia system[1] as shown in Fig. 8. It is obvious that two straight lines are parallel to each other.

Table 3 Values of constants in Eq. (5)[a]

Temp. (°C)	x_{H_2}	η_0	α'	β'	$\gamma'\cdot10^{-3}$
	0.198	105.1	−4.88	597	− 54.7
	0.408	109.2	−1.69	− 114	16.5
25	0.594	111.5	−2.11	701	−150
	0.799	108.7	1.34	−1600	496
	1.000	89.1	0.656	130	0.511
	0.189	113.6	−2.54	104	− 4.55
	0.400	117.6	−3.24	413	− 22.9
50	0.600	119.7	−0.379	− 45.3	− 0.482
	0.794	116.4	0.068	− 504	103
	1.000	94.2	−0.301	334	− 12.4
	0.201	122.8	−1.35	23.7	0.361
	0.398	126.4	−1.06	35.6	− 0.146
75	0.599	127.9	−1.19	177	− 7.28
	0.802	123.0	1.42	− 453	43.7
	1.000	99.0	−0.222	253	− 6.98
	0.202	133.1	−0.977	48.3	− 0.307
	0.404	136.3	−0.397	3.60	1.01
100	0.594	137.5	0.149	− 30.3	2.37
	0.800	131.8	1.09	− 203	16.5
	1.000	104.8	0.291	143	− 4.05

a) $\eta=\eta_0(1+\alpha'\rho+\beta'\rho^2+\gamma'\rho^3)$ η: 10^{-7} Pa·s ρ: 10^3 kg·m^{-3} = g·cm^{-3}

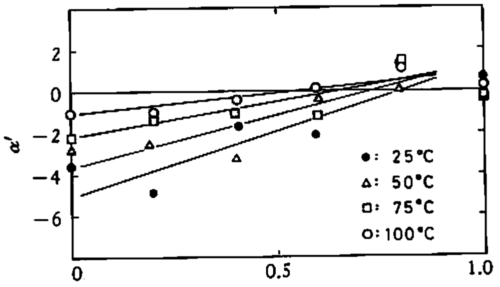

Fig. 7 Relation between α' and mole fraction of hydrogen

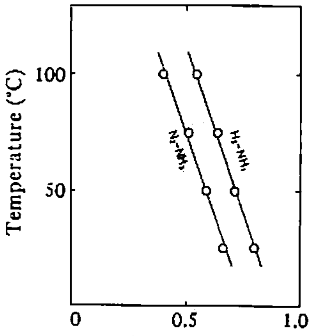

Fig. 8 Relation between temperature and x_n^*

The viscosity of polar gases, such as ammonia, sulfur dioxide, water vapor etc., decreases with an increase in pressure below a certain temperature. It was considered by Stogryn and Hirschfelder[16] that the gas was a mixture of monomers and dimers, and that the initial pressure dependence of viscosity depended on a dimerization effect and a collisional transfer effect. As described in Ref. 1, it can be presumed that polar molecules, such as ammonia, sulfur dioxide etc. form dimers, by considering that water molecules are possible to form dimers[17]. Then, α' for the polar gases is more strongly influenced by the dimerization of their molecules than that for nonpolar gases. Fig. 7 seems to suggest[1] that the rise of temperature and the presence of nonpolar molecules disturb the dimer formation of polar molecules. In addition, from Fig. 8 it may be concluded in these two systems that the nonpolar molecules of larger molecular weight disturb more strongly the dimerization of polar molecules than those of smaller molecular weight.

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