

## **Measurements of the Viscosity of Compressed Gaseous and Liquid Nitrogen + Methane Mixtures**

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The shear viscosity coefficients of three compressed gaseous and liquid nitrogen + methane mixtures have been measured at temperatures between 100 and 300 K and at pressures to about 30 MPa (4350 psia) with a piezoelectric quartz crystal viscometer. The precision of the measurements ranges from about 0.5% at high densities to about 1% at low densities. The estimated experimental error ranges from about 2% at high densities to about 4% at densities near the critical density and at supercritical temperatures near the critical temperature. The measurements have been compared with an extended corresponding states model, previously proposed for calculating the viscosities of fluid mixtures. Differences between the measured and calculated viscosities are discussed.

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**KEY WORDS:** composition dependence; compressed gas; compressed liquid; density dependence; methane; mixtures; nitrogen; piezoelectric crystal viscometer; shear viscosity.

### **1. INTRODUCTION**

Accurate, wide range mathematical models for the behavior of the transport properties of fluids are needed for optimizing transport processes and equipment. As there is no satisfactory molecular theory of the transport properties of dense fluids, much use is made of extended corresponding states models. Accurate, wide range data for carefully selected fluids and their mixtures are useful for validating and improving these models.

There are few accurate viscosity data available for compressed gaseous and liquid mixtures that cover a large *PVT* range. This report presents new absolute shear viscosity coefficient measurements for three nitrogen +

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methane mixtures at temperatures between 100 and 300 K at pressures to about 30 MPa (4350 psia). Nitrogen + methane mixtures have been selected for this study because mixtures containing these components have considerable technological importance, and because considerable information is available for the viscosities of the pure components and for the equilibrium properties of the mixtures. The reduced density and temperature ranges covered here are substantial. Reduced densities range from about 0.1 to 2.7 and reduced temperatures range from about 0.6 to 2.

The dependences of the measured viscosities on density, temperature, and composition have been compared with an extended corresponding states model [1, 2]. Differences between the measured and calculated viscosities are discussed.

## 2. APPARATUS AND PROCEDURES

The measurement method, apparatus, and procedures are essentially the same as we have reported for our work on argon [3], methane [4], and nitrogen [5]. Only details specific to this work are reported here. The same piezoelectric quartz crystal of approximately 5 cm in length and 0.5 cm in diameter, discussed in [3], was used for these measurements.

Viscosities were derived from measured crystal resonance-curve bandwidths using the equation [see ref. 6],

$$\eta = \frac{\pi f}{\rho} \left[ \frac{M}{S} \right]^2 \left[ \frac{\Delta f}{f} - \frac{\Delta f_{\text{vac}}}{f_{\text{vac}}} \right]^2 \quad (1)$$

where  $\rho$  is the fluid density,  $M$  and  $S$  are the mass and surface area of the crystal, and  $f$  and  $\Delta f$  are the resonant frequency and resonance-curve bandwidth of the crystal. This equation has been used to derive all of the viscosities reported from this laboratory. The viscosity measurements were made on the same three mixtures previously prepared gravimetrically and used for *PVT* measurements in this laboratory [7]. The mixture compositions (mole fractions) are summarized in Table I.

**Table I.** Nitrogen + Methane Mixture Compositions Used for Viscosity Measurements

Mixture number	Nitrogen mole fraction	Abbreviated Nitrogen mole fraction, $x_{N_2}$	Methane mole fraction
1	0.50115	0.5	0.49885
2	0.28627	0.3	0.71373
3	0.68341	0.7	0.31659

The highest pressures were obtained by compressing the fluid in the cell, at a temperature well above the fluid critical temperature, with a commercially available diaphragm type compressor. Care was taken to keep the pressure well above the critical pressure of the mixture while cooling the cell below the critical temperature of the mixture.

Densities are required to obtain viscosities from Eq. (1) and to examine the dependence of the viscosity on the density. Densities were obtained from measured temperatures and pressures and a mathematical model for the *PVT* properties of nitrogen + methane mixtures. An extended corresponding states model [8] was used to calculate the densities of compressed gaseous 0.50115 nitrogen + 0.49885 methane at densities smaller than  $8 \text{ mol} \cdot \text{liter}^{-1}$ . The error in these calculated densities is believed to be less than 2%. A 32 term modified BWR equation was used to calculate the densities of this composition at gas densities larger than  $8 \text{ mol} \cdot \text{liter}^{-1}$  and at liquid densities. The BWR equation was optimized [9] to the measured *PVT* properties of this composition [7] as if it were a pure fluid. The error in these calculated densities is believed to be less than 0.2%. The extended corresponding states model [8] was used to calculate all of the densities of compressed gaseous and liquid 0.28627 nitrogen + 0.71373 methane and of 0.68341 nitrogen + 0.31659 methane. The error in these calculated densities is believed to be less than 0.5%, except at densities near the critical density and at our experimental supercritical temperature nearest the critical temperature, where the error is believed to be as large as 2% [7].

### 3. RESULTS AND DISCUSSION

Measurements of the viscosities of compressed gaseous and liquid 0.50115 nitrogen + 0.49885 methane are presented in Table II and Fig. 1. Measurements of the viscosities of compressed gaseous and liquid 0.28627 nitrogen + 0.71373 methane are presented in Table III and Fig. 2. Measurements of the viscosity of compressed gaseous and liquid 0.68341 nitrogen + 0.31659 methane are presented in Table IV and Fig. 3. All of the measurements were made at temperatures between 100 and 300 K and at pressures to 30 MPa (4350 psia). The estimated precision of the measurements ranges from 0.5% at high densities to 1% at low densities. The experimental error is believed to be less than 2%, except at densities near the critical density and at our supercritical temperature nearest the critical temperature, where errors in the calculated densities may produce viscosity errors as large as 4%.

The dependences of the mixture viscosities on density and temperature at fixed composition, shown in Figs. 1–3, are similar to the density and temperature dependences obtained for the pure components [4, 5]. At high



Table II. (Continued)

$P$ (MPa)	$\rho$ (mol · Liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )	$P$ (MPa)	$\rho$ (mol · Liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )
$T = 170.00 \text{ K}$			$T = 120.00 \text{ K}$		
6.5236	11.2345	196.0	33.8660	26.7969	1055.1
6.2972	10.5478	184.3	30.1290	26.5492	1020.7
6.0300	9.6681	169.1	26.5600	26.2969	979.6
5.8241	8.9550	158.5	23.2849	26.0495	949.1
5.5367	7.9587	146.3	19.9239	25.7770	915.2
5.3123	7.2299	136.3	15.6289	25.3950	843.7
4.8044	5.8659	121.8	12.8348	25.1210	815.7
4.4859	4.9497	118.9	9.3648	24.7437	770.4
3.7894	3.7723	108.6	5.7291	24.2881	721.7
3.0886	2.8257	103.5	2.5177	23.8077	677.7
2.3257	1.9694	97.0			
1.6957	1.3583	94.9			
$T = 155.00 \text{ K}$			$T = 110.00 \text{ K}$		
31.8596	23.4123	627.3	30.8632	27.5119	1240.5
28.2060	23.0064	597.2	28.0773	27.3444	1200.4
23.4197	22.3907	553.3	24.6574	27.1288	1162.7
17.8921	21.5025	498.5	21.3706	26.9097	1106.2
14.4767	20.7986	462.9	17.7256	26.6507	1065.1
10.8686	19.8175	423.0	14.8891	26.4353	1034.9
8.8518	19.0700	382.8	10.8518	26.1027	977.7
7.3990	18.3549	361.1	7.9721	25.8421	926.2
6.5603	17.8167	344.0	4.5678	25.5003	877.9
5.8142	17.1923	324.7	1.7003	25.1737	834.8
5.1514	16.4000	316.4			
$T = 140.00 \text{ K}$			$T = 100.00 \text{ K}$		
30.9548	24.7393	761.1	30.3398	28.3808	1522.4
27.4193	24.4138	727.4	27.4612	28.2300	1473.3
24.7171	24.1431	700.2	24.6142	28.0755	1421.7
21.3083	23.7684	667.2	21.4048	27.8942	1385.6
17.7402	23.3253	627.7	17.8226	27.6813	1322.5
14.1914	22.8143	590.1	14.3200	27.4604	1276.2
10.7319	22.2162	544.8	10.7847	27.2218	1218.6
7.4535	21.4990	501.3	7.9954	27.0197	1162.9
4.0007	20.4124	446.6	5.2236	26.8039	1135.3
			2.3620	26.5611	1073.4

densities (larger than  $2\rho_c$ ) the viscosity increases strongly with increasing density at fixed temperature and decreases weakly with increasing temperature at fixed density.

There are few other viscosity measurements reported for compressed gaseous and liquid nitrogen + methane mixtures in the same  $PVT$  range.

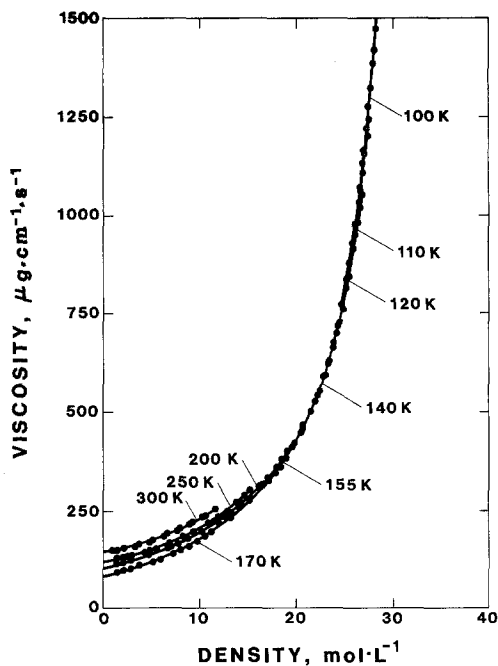


Fig. 1. Viscosity of compressed gaseous and liquid 0.50115 nitrogen + 0.49885 methane as a function of density.

Table III. Viscosity of Compressed Gaseous and Liquid 0.28627 Nitrogen + 0.71373 Methane Mixture

$P$ (MPa)	$\rho$ (mol · liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )	$P$ (MPa)	$\rho$ (mol · liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )
$T = 300.00 \text{ K}$			$T = 250.00 \text{ K}$		
30.7863	12.2731	248.7	30.2514	15.4520	292.9
28.0996	11.5152	238.5	27.5526	14.7154	275.7
24.6274	10.4237	219.5	24.8019	13.8541	260.1
22.0291	9.5148	208.5	22.0241	12.8395	237.5
19.1767	8.4222	196.0	19.2155	11.6222	218.7
16.3318	7.2393	181.0	16.4483	10.1860	196.4
14.2296	6.3162	170.4	14.0684	8.7446	176.8
12.1500	5.3745	161.6	12.2836	7.5591	164.5
9.9904	4.3851	152.2	10.1173	6.0630	146.5
7.8531	3.4049	145.1	8.0659	4.6633	135.4
5.8242	2.4855	139.1	5.9232	3.2761	124.6
3.7992	1.5902	131.6	3.8265	2.0168	118.4
1.6924	.6922	125.1	1.7026	.8529	114.3

Pressure =  $P$ ; density =  $\rho$ ; viscosity =  $\eta$ .

Table III. (Continued)

$P$ (MPa)	$\rho$ (mol · liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )	$P$ (MPa)	$\rho$ (mol · liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )
$T = 200.00 \text{ K}$			$T = 140.00 \text{ K}$		
30.8132	19.9616	427.1	6.0203	22.6717	583.5
28.0943	19.4998	408.8	3.2294	22.1680	542.6
25.5596	19.0119	388.6			
22.8598	18.4110	365.0	$T = 120.00 \text{ K}$		
19.9453	17.6293	342.9	30.6724	26.8983	1145.9
17.1115	16.6659	314.7	28.2007	26.7576	1118.1
14.5695	15.5154	286.3	24.5270	26.5376	1064.0
12.3872	14.1369	255.3	21.4332	26.3413	1033.3
11.0525	12.9793	232.4	17.9183	26.1042	1003.6
10.1198	11.9453	220.3	14.1964	25.8346	954.2
8.7916	10.0387	191.1	10.7717	25.5666	920.1
7.4029	7.6204	155.7	8.1137	25.3429	873.7
5.9159	5.2771	133.0	5.2819	25.0864	847.5
4.5222	3.5867	114.3	1.8306	24.7421	794.7
3.0991	2.2204	103.4			
1.6029	1.0483	98.1	$T = 110.00 \text{ K}$		
			30.1293	27.6954	1375.5
			27.5805	27.5675	1336.7
			24.7712	27.4206	1300.0
			21.3994	27.2356	1248.1
			17.8268	27.0283	1203.7
			14.4708	26.8222	1149.4
			11.5837	26.6350	1118.3
			8.6663	26.4356	1072.6
			5.1092	26.1765	1032.5
			1.7905	25.9165	985.4
			$T = 100.00 \text{ K}$		
			29.6496	28.4817	1732.8
			27.3669	28.3822	1692.9
			24.7275	28.2629	1635.0
			21.5589	28.1133	1583.1
			17.7079	27.9218	1536.8
			14.3388	27.7450	1470.3
			10.5610	27.5359	1397.7
			7.9629	27.3850	1354.3
			5.1503	27.2148	1318.2
			2.3216	27.0360	1257.6
$T = 165.00 \text{ K}$					
31.5995	23.1538	616.3			
28.1512	22.7986	590.8			
24.7215	22.4057	556.6			
21.4090	21.9773	527.7			
17.7757	21.4314	494.1			
14.4679	20.8328	458.4			
11.9933	20.2867	434.9			
8.9718	19.4228	396.3			
7.4127	18.8240	372.8			
5.8977	18.0371	346.0			
$T = 140.00 \text{ K}$					
30.7776	25.2228	839.1			
28.2703	25.0374	818.4			
24.7465	24.7595	777.8			
21.3095	24.4654	740.1			
17.8751	24.1436	710.5			
14.3567	23.7773	680.3			
11.6627	23.4643	644.7			
8.8425	23.0964	613.2			

The capillary tube measurements of Gnezdilov and Golubev [10] on compressed gaseous 0.449 nitrogen + 0.551 methane at 298.15 K were compared with our measurements on 0.50115 nitrogen + 0.49885 methane at 300 K by comparing both sets of measurements to an extended corresponding states model [1,2]. The measurements appear to be consistent within the combined experimental errors. By contrast, the oscillating cylin-

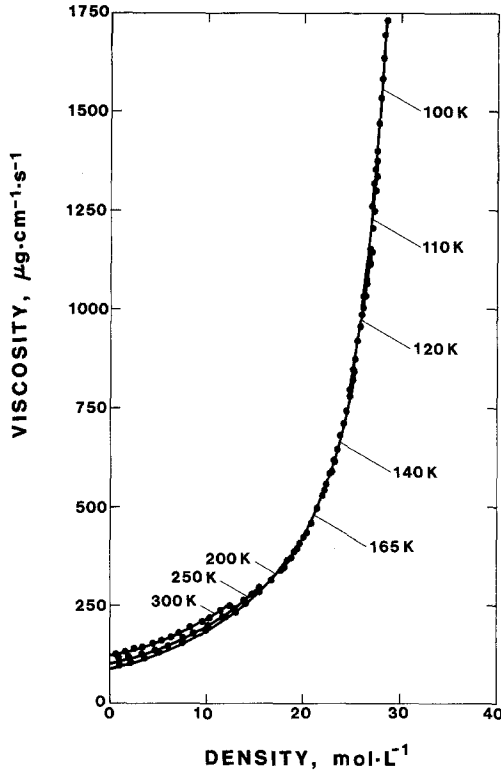


Fig. 2. Viscosity of compressed gaseous and liquid 0.28627 nitrogen + 0.71373 methane as a function of density.

der measurements of Gerf and Galkov [11] on liquid 0.494 nitrogen + 0.506 methane were compared with our measurements on liquid 0.50115 nitrogen + 0.49885 methane and were found to be about 20–30% larger.

The measurements reported in Tables II–IV have been compared with an extended corresponding states model [1,2], previously proposed for calculating the viscosities of fluid mixtures throughout a wide range of  $PVTx$  states. The model makes use of a methane reference state to calculate the viscosities of the other components, and is predictive in the sense that it does not make use of mixture viscosity data. Most of the differences between our measurements on compressed gaseous nitrogen + methane mixtures and the model are within our estimated experimental error and will not be discussed further here. Most of the differences between our measurements on compressed liquid nitrogen + methane mixtures are larger than our estimated experimental error and smaller than the estimated uncertainties of the model [1,2]. The differences between our



**Table IV.** Viscosity of Compressed Gaseous and Liquid 0.68341  
Nitrogen + 0.31659 Methane Mixture

$P$ (MPa)	$\rho$ (mol · liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )	$P$ (MPa)	$\rho$ (mol · liter <sup>-1</sup> )	$\eta$ ( $\mu\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ )
$T = 300.00 \text{ K}$			$T = 140.00 \text{ K}$		
31.2346	11.4102	260.9	32.6452	24.5732	739.1
28.1067	10.5499	248.1	30.4744	24.3458	716.6
25.4813	9.7717	238.3	28.0345	24.0733	697.5
22.8188	8.9266	229.2	24.5507	23.6464	652.5
20.0590	7.9899	216.2	21.4211	23.2151	623.2
17.0725	6.9081	204.2	17.9195	22.6596	575.9
14.4482	5.9040	192.9	14.3347	21.9744	528.5
13.1287	5.3827	190.1	11.6594	21.3428	489.6
10.9474	4.5113	179.6	8.9251	20.5136	452.8
8.8114	3.6376	172.0	6.1444	19.2747	398.4
6.6221	2.7289	165.0			
4.5659	1.8720	159.0		$T = 120.00 \text{ K}$	
1.7686	0.7164	155.3	31.0056	26.4252	978.4
			27.9432	26.1726	948.6
			24.6056	25.8766	897.3
			21.3729	25.5656	861.9
			17.8467	25.1927	824.7
	$T = 250.00 \text{ K}$		13.6544	24.6896	766.0
30.3905	13.9433	284.7	11.6422	24.4178	736.2
27.5872	13.1081	269.0	8.8198	23.9915	698.7
24.7297	12.1576	253.3	5.9909	23.4908	653.8
21.3672	10.8872	232.6	3.1330	22.8673	609.2
18.2968	9.5636	212.4			
15.7249	8.3310	198.3		$T = 110.00$	
12.8263	6.8252	180.8	29.7748	27.3443	1156.6
10.0876	5.3288	168.6	27.4845	27.1786	1128.5
7.3391	3.8246	154.1	24.7182	26.9682	1086.7
4.5374	2.3080	142.7	22.1662	26.7629	1047.5
1.6521	0.8125	138.2	18.0791	26.4086	989.5
			14.5707	26.0742	944.2
			11.5888	25.7624	897.3
			8.7905	25.4409	853.9
			5.9531	25.0781	816.5
			2.2632	24.5281	751.6
	$T = 200.00 \text{ K}$			$T = 100.00 \text{ K}$	
33.5588	18.8541	397.1	30.9526	28.4244	1420.7
31.0638	18.3179	380.5	28.2375	28.2583	1391.1
28.3282	17.6560	358.0	24.6603	28.0270	1335.2
25.5660	16.8878	337.1	21.5045	27.8100	1279.0
22.9169	16.0277	314.1	17.9260	27.5476	1225.8
19.9803	14.8827	289.5	14.5691	27.2833	1173.4
17.5355	13.7164	266.4	10.8072	26.9629	1110.4
14.4413	11.8394	231.9	8.1101	26.7144	1072.4
12.2766	10.1729	213.0	5.1829	26.4232	1018.7
10.0921	8.1981	183.5	2.4493	26.1265	968.3
7.9643	6.1592	163.8			
5.8229	4.2277	145.5			
3.7634	2.5580	128.8			
1.6770	1.0641	119.3			

Pressure =  $P$ ; density =  $\rho$ ; viscosity =  $\eta$ .

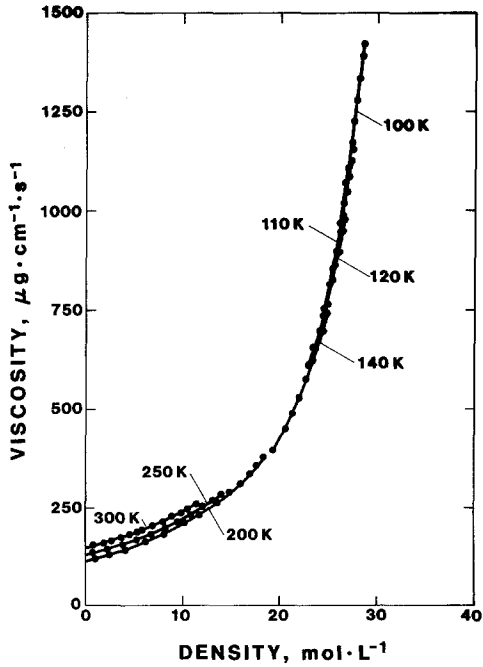


Fig. 3. Viscosity of compressed gaseous and liquid 0.68341 nitrogen + 0.31659 methane as a function of density.

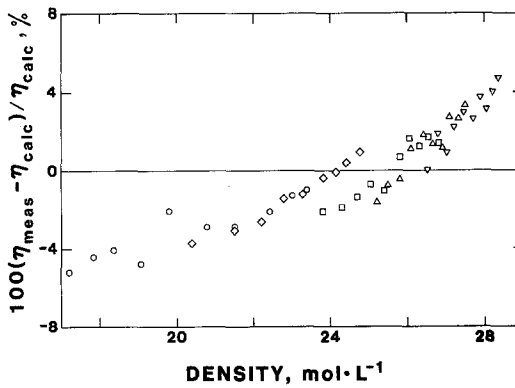


Fig. 4. Comparison of measured viscosities of compressed liquid 0.50115 nitrogen + 0.49885 methane with the extended corresponding states model [1, 2]. The temperatures are 155 K, ○; 140 K, ◇; 120 K, □; 110 K, △; and 100 K, ▽.

measurements on compressed liquid 0.50115 nitrogen + 0.49885 methane and the model are shown in Fig. 4. The largest differences are about 5%, and there are noticeable dependences on density and temperature. The dependence of the measured viscosities on density at fixed temperature is a little stronger than that given by the model. The differences are weakly dependent on temperature at fixed density. The differences between the measured and calculated viscosities, and the dependences of the differences on density and temperature, are similar for the other mixture compositions. The largest differences, up to 8%, were obtained for 0.68341 nitrogen + 0.31659 methane at the highest density.

Measurements of the viscosities of the three compressed liquid nitrogen + methane mixtures, and of the pure components [4, 5], all at high densities (25.0–28.6 mol · liter<sup>-1</sup>) and the same temperature (100 K), are shown in Fig. 5. The viscosity clearly decreases with increasing nitrogen concentration at fixed molar density and at fixed temperature. The dependence of the measured viscosities on composition at fixed molar density (28.0 mol · liter<sup>-1</sup>) and at fixed temperature (100 K) is shown in Fig. 6. The measured viscosity is smaller than the mole fraction average of the pure

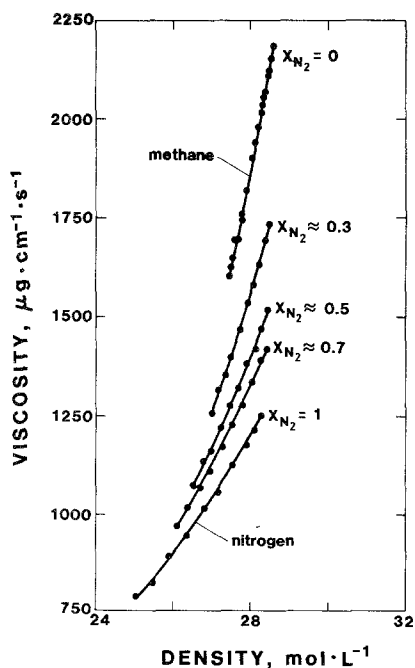


Fig. 5. Viscosity of compressed liquid nitrogen + methane mixtures and their pure components as a function of molar density at fixed temperature (100 K).

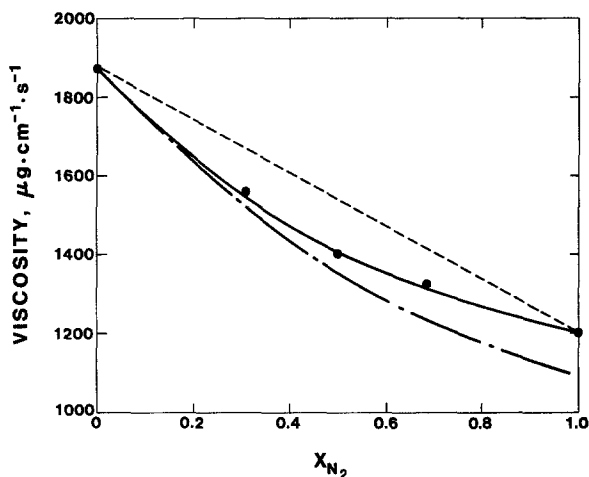


Fig. 6. Viscosity of compressed liquid nitrogen + methane mixtures and their pure components as a function of composition at fixed molar density ( $28.0 \text{ mol} \cdot \text{liter}^{-1}$ ) and at fixed temperature (100 K). The present measurements, ●; mole fraction average of the pure component viscosities, ---; extended corresponding states model [1, 2], - · - · -.

components, and the largest difference between them is about 10%. Calculated viscosities, obtained from the extended corresponding states model [1, 2], at the same compositions, density, and temperature, are shown in Fig. 6 for comparison. As the measured viscosity of pure liquid methane at  $28.0 \text{ mol} \cdot \text{liter}^{-1}$  and 100 K [4] is about 9% larger than that given by the methane reference state, and the viscosity of pure liquid nitrogen at  $28.0 \text{ mol} \cdot \text{liter}^{-1}$  and 100 K [5] is about 15% larger than that given by the model, all of the calculated viscosities have been multiplied by the ratio of the measured to calculated viscosities of pure methane at  $28.0 \text{ mol} \cdot \text{liter}^{-1}$  and 100 K to focus on the composition dependence. The calculated viscosity of pure liquid nitrogen is still about 9% smaller than the measured value. This difference is believed due mainly to poor correspondence between the viscosities of liquid nitrogen and liquid methane at high reduced densities [5]. The calculated composition dependence is quite similar to the measured composition dependence at fixed density and temperature.

#### 4. SUMMARY

New absolute viscosity measurements have been reported for three compressed gaseous and liquid nitrogen + methane mixtures throughout a wide range of *PVT* states. The dependences of the viscosities on density

and temperature at fixed composition, and on composition at fixed molar density and temperature, have been examined. The dependences on density and temperature are similar to those obtained for the pure components. The measurements have been compared with an extended corresponding states model, previously proposed for calculating the viscosities of mixtures of nonpolar fluids throughout a wide range of *PVT* states. The model gives a good account of the dependences on density, temperature, and composition. The largest differences between measured and calculated mixture viscosities are less than 8%. Much of the difference is believed to be due to the poor correspondence between the viscosities of pure liquid nitrogen and pure liquid methane at high reduced densities.

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