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Measurements of the Viscosity of Compressed Gaseous and Liquid Methane + Ethane Mixtures

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The shear viscosity coefficients of three compressed gaseous and liquid methane + ethane 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 0.5% to about 2%, depending on the density × viscosity range. The experimental error is estimated to be less than 2% in most cases. The measurements have been compared with other data, and with a multiparameter extended corresponding states model, previously proposed for calculating the viscosities of fluid mixtures throughout a wide range of *PVT* states.

Introduction

There are few shear viscosity data available for compressed gaseous and liquid mixtures throughout a large *PVT* range. We have recently reported such measurements for nitrogen + methane mixtures (*1*). Here we report shear viscosity measurements for compressed gaseous and liquid methane + ethane mixtures at temperatures between 100 and 300 K and at pressures to 30 MPa (4350 psia). We have previously reported viscosity measurements for the pure components in this range (*2*, *3*). The measurements reported here, together with those for the pure components, permit examination of the dependences of the viscosities on density, temperature, and composition over a substantially larger viscosity range than was possible for nitrogen + methane. The measurements have been compared with a multiparameter extended corresponding state model (*4*, *5*), previously proposed for calculating the viscosities of nonpolar fluid mixtures throughout a large *PVT* range.

Apparatus and Procedures

The measurement method, apparatus, and procedures are essentially the same as we have reported for our work on argon (*6*), methane (*2*), and ethane (*3*). The same piezoelectric quartz crystal of approximately 5-cm length and 0.5-cm diameter discussed in ref *6* was used for these measurements. Viscosities were derived from measured crystal resonance-curve bandwidths by using the equation (*7*)

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

where ρ is the fluid density, M is the mass and S is the surface area of the crystal adjusted for thermal expansion and hydrostatic compression, and f and Δf are the resonant frequency and resonance-curve bandwidth of the crystal in the fluid.

The viscosity measurements were made on the same three mixture compositions which were prepared gravimetrically and used for *PVT* measurements in this laboratory (*8*). The mixture compositions are summarized in Table I.

Table I. Methane + Ethane Mixture Compositions (Mole Fractions)

mixture	[CH_4], mole fraction	[C_2H_6], mole fraction
1	0.502 17	0.497 83
2	0.685 26	0.314 74
3	0.345 28	0.654 72

All of the liquid-phase viscosity measurements were made on essentially one sample for each composition. The gas was compressed at ambient temperature to a pressure well above the critical pressure of the mixture with a commercial diaphragm compressor. The cell was then cooled below the critical temperature of the mixture, care being taken to keep the pressure well above the critical pressure by adding additional gas if necessary. During each isothermal measurement run gas was vented at fixed cell temperature to obtain a series of densities. After a run the cell temperature was increased to the next run temperature and gas was added to obtain the starting pressure and density.

Fluid densities were obtained from measured temperatures and pressures and an equation of state. At temperatures above the critical temperature of the mixture, densities were obtained from a 32-term modified BWR equation fit to the measured *PVT* properties of each composition as if it were a pure fluid (*8*). The error in these calculated densities is estimated to be less than 0.2%. At temperatures below the critical temperature of the mixture, densities were obtained from an extended corresponding states model for the *PVT* properties of mixtures, optimized mainly to measured saturated liquid densities (*9*). The error in these calculated densities is also estimated to be less than 0.2% at our experimental temperatures and pressures.

Results and Discussion

Presentation of Results and Error Estimates. Measurements of the viscosities of compressed gaseous and liquid methane + ethane are presented in Tables II-IV and Figures 1-3. The mixture compositions are given in Table I; and densities range from 0.7 to 26 mol·L^{-1} at temperatures between 100 and 300 K and at pressures to 30 MPa. The measurement method and our apparatus have been validated previously, mainly by comparisons between our measurements on compressed gaseous and liquid argon and measurements on argon by other workers using other methods (*6*). Comparisons on argon have been supplemented by additional comparisons on other fluids with similar results (*2*, *10*). The imprecision of the measurements presented here ranges from less than 2% at the lowest densities to 0.5% at intermediate densities and about 1% at the highest densities. The experimental error is estimated to be less than 2% in most cases.

Comparisons with Other Measurements on Methane + Ethane Mixtures. Figure 4 shows a comparison of our measurements on compressed gaseous methane + ethane at 300.00 K with the oscillating disk measurements of Abe et al.

Table II. Viscosity of Compressed Gaseous and Liquid 0.502 17 Methane + 0.497 83 Ethane

P, MPa	ρ, mol·L^{-1}	η, μg·cm^{-1}·s^{-1}	P, MPa	ρ, mol·L^{-1}	η, μg·cm^{-1}·s^{-1}
Gas, T = 300.00 K					
34.8592	15.381	482.7	8.9451	6.051	162.6
29.4071	14.669	437.9	7.9121	4.994	147.6
24.3306	13.806	395.8	6.5226	3.729	130.5
20.6932	12.983	357.0	5.5301	2.956	120.0
17.1946	11.894	312.8	5.0240	2.599	120.0
14.8908	10.887	279.2	4.9994	2.582	118.8
13.4153	10.039	253.1	3.9057	1.889	109.7
12.1703	9.149	229.7	3.7185	1.780	110.3
10.8330	7.983	202.3	1.7571	0.760	106.8
9.9574	7.112	184.9	1.6687	0.719	109.3
Gas, T = 280.00 K					
32.2466	16.144	522.7	8.0980	7.425	179.5
23.0315	14.920	446.6	7.3119	6.088	150.3
18.8297	14.100	399.4	6.4729	4.787	131.6
15.1154	13.063	349.6	5.6596	3.762	119.4
12.3275	11.847	299.4	4.8610	2.954	110.1
11.0413	11.002	268.7	3.3240	1.758	104.1
9.4757	9.463	229.2	1.6815	0.793	99.2
8.8117	8.561	205.4			
Liquid, T = 250.00 K					
31.1336	17.593	648.6	17.9601	16.222	523.9
28.2235	17.347	626.7	14.5367	15.686	483.3
24.8270	17.028	592.2	11.1389	14.981	434.0
21.5116	16.672	557.3	7.6254	13.825	369.1
Liquid, T = 200.0 K					
30.3027	20.128	1014.7	14.4433	19.226	860.5
28.2156	20.026	994.1	11.0177	18.982	824.9
24.7066	19.843	964.5	7.5165	18.701	791.3
22.1131	19.701	938.1	4.0647	18.385	740.8
17.6046	19.433	915.4			
Liquid, T = 170.00 K					
31.9803	21.674	1401.0	13.8659	20.952	1229.2
28.3672	21.545	1374.0	10.8430	20.813	1189.8
24.8037	21.410	1341.6	8.0962	20.680	1158.7
21.6272	21.285	1306.0	4.6887	20.504	1128.5
17.9870	21.133	1275.4	1.9149	20.352	1079.3
Liquid, T = 150.00 K					
30.4402	22.571	1849.0	14.5773	22.065	1641.7
28.1086	22.503	1816.1	11.0294	21.937	1600.6
24.8676	22.404	1799.6	8.2222	21.833	1549.0
21.5572	22.300	1762.0	5.2078	21.716	1507.9
17.8794	22.178	1696.9	1.6655	21.574	1478.0
Liquid, T = 130.00 K					
31.0199	23.484	2616.7	14.4679	23.078	2257.0
28.3683	23.425	2527.5	11.0395	22.984	2226.2
24.8162	23.341	2475.5	8.2121	22.904	2176.3
21.4867	23.260	2423.3	4.7619	22.803	2118.1
17.9532	23.171	2354.6	1.7454	22.712	2056.1
Liquid, T = 120.00 K					
30.6070	23.897	3196.9	14.4897	23.562	2821.3
28.2165	23.851	3102.5	10.9532	23.480	2731.1
24.8050	23.783	3060.1	7.3356	23.392	2650.5
21.3735	23.713	2961.5	4.0357	23.310	2605.1
17.9198	23.638	2913.2	1.5450	23.246	2527.3
Liquid, T = 110.00 K					
30.7987	24.301	4058.9	14.5986	24.027	3548.5
28.3015	24.262	3994.2	11.1004	23.962	3473.9
24.7990	24.206	3893.1	8.9728	23.920	3413.2
23.4616	24.183	3847.9	7.4467	23.890	3391.1
21.4830	24.150	3779.2	4.5325	23.832	3325.2
17.9296	24.088	3633.0	1.6681	23.773	3234.1
16.1116	24.055	3576.2			
Liquid, T = 105.00 K					
31.0769	24.499	4743.3	14.3931	24.249	4052.8
28.3107	24.460	4643.6	9.7168	24.171	3914.6
24.8431	24.411	4457.3	5.3770	24.095	3768.9
21.4838	24.361	4362.4	1.8045	24.031	3655.6
17.9135	24.305	4240.1			

Table II (*Continued*)

P, MPa	ρ, mol·L^{-1}	η, µg·cm^{-1}·s^{-1}	P, MPa	ρ, mol·L^{-1}	η, µg·cm^{-1}·s^{-1}
		Liquid, T = 100.00 K			
31.7087	24.697	5657.4	14.2173	24.469	4897.7
28.4606	24.658	5499.9	10.9931	24.422	4751.8
25.0000	24.614	5346.3	7.4825	24.370	4508.7
21.6622	24.570	5194.5	4.6572	24.327	4417.0
18.1704	24.524	5038.5	1.7612	24.282	4326.4

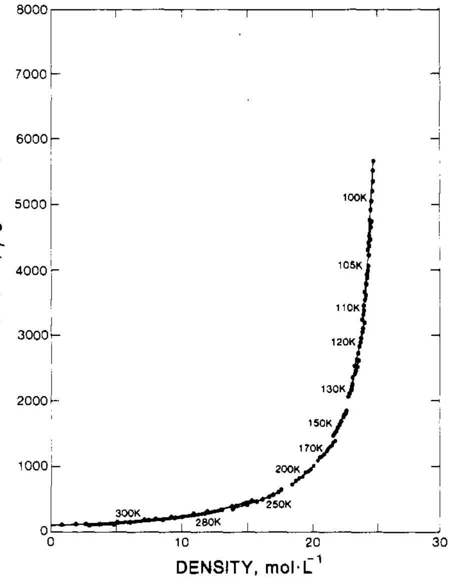

Figure 1. Viscosity of compressed gaseous and liquid 0.502 17 methane + 0.497 83 ethane as a function of density.

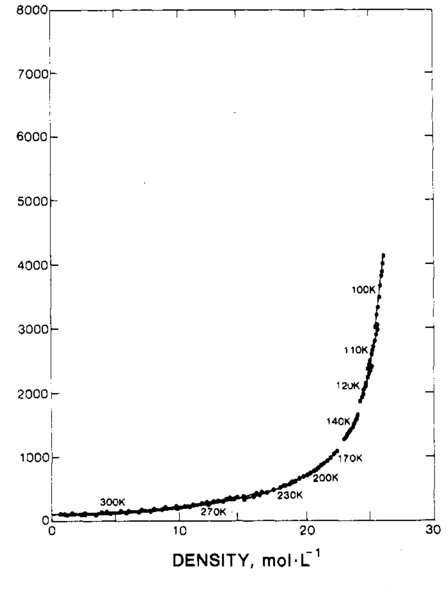

Figure 2. Viscosity of compressed gaseous and liquid 0.685 26 methane + 0.314 74 ethane as a function of density.

(*11*) on the low-pressure gas at 298.15 K. As the two sets of measurements were made on slightly different compositions, and at different temperatures and pressures, they have been compared with each other by comparing both sets with an extended corresponding states model (*4*, *5*). Figure 4 shows that the two sets of measurements are consistent with each other within the combined experimental error. We are not aware of any other viscosity measurements on methane + ethane mixtures within the temperature and pressure ranges of this work.

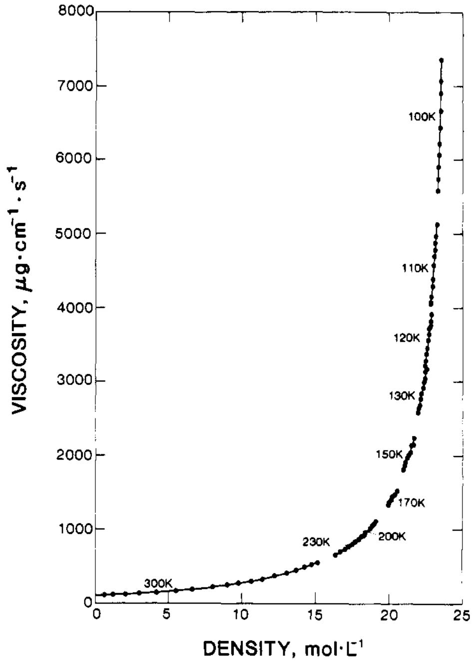

Figure 3. Viscosity of compressed gaseous and liquid 0.345 28 methane + 0.654 72 ethane as a function of density.

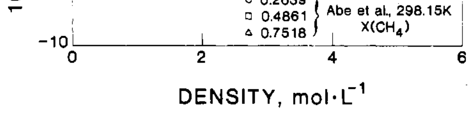

Figure 4. Comparison of viscosity measurements on gaseous methane + ethane mixtures with the measurements of Abe et al. (*11*).

Comparisons with an Extended Corresponding States Model. All of the viscosity measurements have been compared with an extended corresponding states model (*4*, *5*), previously proposed by Ely and Hanley for calculating the viscosities of nonpolar mixtures throughout a wide range of *PVT* states. Contributions to the development of corresponding states models for the transport properties of mixtures have also been made by Gubbins and co-workers (*12*). Figure 5 shows the differences between measured and calculated viscosities for the 0.345 28 methane + 0.654 72 ethane mixture. At low densities ($\rho < \rho_c$) the measurements and the model differ by up to 5%. At intermediate densities ($\rho_c < \rho < 2\rho_c$), the differences are smaller than our experimental error. At high

Table III. Viscosity of Compressed Gaseous and Liquid 0.685 26 Methane + 0.314 74 Ethane

P, MPa	ρ, mol·L^{-1}	η, μg·cm^{-1}·s^{-1}	P, MPa	ρ, mol·L^{-1}	η, μg·cm^{-1}·s^{-1}
Gas, T = 300.00 K					
31.5549	14.623	366.8	14.3713	8.890	205.1
31.2549	14.569	363.1	13.0252	7.990	189.5
28.1718	13.971	340.1	11.8228	7.122	169.3
26.9964	13.715	328.8	10.3676	6.028	155.9
25.6552	13.400	320.2	9.5907	5.444	147.9
24.1344	13.007	308.6	8.0179	4.301	134.1
22.8849	12.651	298.5	7.5270	3.962	131.4
21.3870	12.178	283.7	5.1580	2.471	118.4
20.2121	11.764	270.9	5.3783	2.599	119.8
18.4726	11.065	253.7	3.5724	1.612	115.4
17.0971	10.427	240.5	2.5441	1.109	111.6
15.7916	9.739	222.6	1.6010	0.677	113.4
Gas, T = 270.00 K					
31.8276	16.527	443.5	10.1575	8.701	190.9
28.3682	16.023	416.9	9.3775	7.257	164.1
25.7125	15.573	395.5	8.6714	6.859	154.0
22.8115	14.994	369.0	7.9163	5.906	141.8
19.8358	14.255	339.5	6.7674	4.584	126.0
17.2243	13.426	313.9	5.6319	3.479	116.6
14.5716	12.263	274.5	4.5445	2.591	109.3
12.2492	10.752	231.8	2.4143	1.208	101.5
11.1820	9.801	210.0			
Liquid, T = 230.00 K					
31.1590	18.933	601.2	14.5316	16.847	448.0
28.3101	18.671	576.8	12.3612	16.382	420.5
24.8585	18.318	551.1	10.2038	15.799	390.4
21.5537	17.932	518.2	8.2314	15.071	350.8
17.8994	17.426	487.0			
Liquid, T = 200.00 K					
31.2625	20.726	796.8	14.4639	19.416	650.4
28.3689	20.539	768.0	16.6887	19.118	613.4
24.9453	20.302	741.3	8.6014	18.736	577.5
21.4976	20.042	711.0	5.1123	18.201	531.8
17.9607	19.746	675.4			
Liquid, T = 170.00 K					
30.7809	22.423	1081.5	14.4312	21.565	931.1
28.3801	22.311	1078.7	11.2627	21.364	894.0
24.8905	22.141	1035.8	8.1074	21.150	857.9
21.5573	21.969	1011.9	4.9574	20.916	827.8
17.9102	21.769	971.2	2.7334	20.737	803.2
Liquid, T = 140.00 K					
29.1487	24.025	1631.3	14.2190	23.471	1414.2
26.9196	23.949	1579.1	10.9203	23.333	1392.2
24.7019	23.871	1562.0	8.0905	23.211	1360.5
21.3819	23.750	1504.2	5.1194	23.077	1312.0
17.8569	23.161	1457.1	2.5722	22.958	1269.1
Liquid, T = 120.00 K					
32.8713	25.168	2392.5	14.4692	24.658	2079.9
29.0185	25.070	2367.4	10.8944	24.545	2018.1
24.8557	24.960	2283.7	7.4523	24.433	1957.0
21.5062	24.866	2232.7	5.1217	24.354	1907.7
18.0968	24.768	2139.0	3.0830	24.284	1851.5
Liquid, T = 110.00 K					
30.5362	25.594	3056.3	13.8427	25.197	2654.3
28.2733	25.545	2973.3	10.9512	25.120	2594.6
24.6949	25.464	2902.9	8.0421	25.041	2496.7
21.4408	25.388	2800.0	5.0368	24.955	2439.2
17.8531	25.300	2719.9	2.3441	24.877	2351.2
Liquid, T = 100.00 K					
31.6842	26.072	4137.2	14.4031	25.744	3472.1
28.2708	26.013	4009.9	10.8216	25.667	3351.9
24.7857	25.949	3894.3	7.8697	25.602	3311.4
21.5235	25.887	3822.5	5.0391	25.538	3209.5
17.9678	25.817	3663.7	2.4204	25.477	3006.4

Table IV. Viscosity of Compressed Gaseous and Liquid 0.345 28 Methane + 0.654 72 Ethane

P, MPa	ρ, mol·L^{-1}	η, μg·cm^{-1}·s^{-1}	P, MPa	ρ, mol·L^{-1}	η, μg·cm^{-1}·s^{-1}
Gas, T = 300.00 K					
31.7305	15.103	546.6	9.5977	8.954	242.0
28.1588	14.706	517.0	8.8533	8.000	216.3
24.7319	14.258	483.2	7.9140	6.559	178.5
21.3742	13.725	450.6	7.2674	5.533	155.4
17.8400	13.004	408.5	6.2898	4.179	135.5
15.0269	12.218	364.4	5.0998	2.938	124.2
12.8830	11.373	325.9	3.8739	1.987	113.1
11.4958	10.604	296.7	2.5673	1.195	107.4
10.3631	9.735	267.1	1.5585	0.683	101.3
Liquid, T = 230.00 K					
32.1116	18.334	941.4	14.3328	17.205	770.0
28.5824	18.147	913.4	11.6409	16.973	733.8
24.8129	17.931	870.0	8.7480	16.691	702.4
21.4970	17.725	843.5	5.9254	16.369	657.4
17.8813	17.477	802.4			
Liquid, T = 200.00 K					
19.8197	19.151	1104.4	15.0643	18.918	1059.5
17.9241	19.016	1093.7	12.2209	18.768	1018.4
15.0643	18.918	1059.5	9.2152	18.598	999.3
12.2209	18.768	1018.4	6.4597	18.430	964.8
19.8197	19.151	1104.4	3.4883	18.235	917.2
17.9241	19.061	1093.7			
Liquid, T = 170.00 K					
17.8203	20515	1538.4	8.2581	20.164	1411.5
14.4489	20.396	1492.8	5.1575	20.040	1385.0
10.9173	20.266	1445.6	2.4271	19.926	1343.6
Liquid, T = 150.00 K					
27.3246	21.677	2212.0	11.7381	21.258	1962.1
24.6997	21.612	2165.7	8.8709	21.172	1912.9
21.5275	21.530	2128.2	6.0025	21.084	1854.5
17.9318	21.433	2037.4	2.3193	20.967	1805.7
14.5272	21.338	2012.2			
Liquid, T = 130.00 K					
29.9927	22.524	3168.2	14.4477	22.221	2838.4
28.2819	22.493	3143.3	12.1513	22.171	2765.8
24.8067	22.429	3032.8	8.6928	22.095	2677.9
21.5206	22.365	2992.3	5.8982	22.031	2654.6
17.9394	22.293	2908.9	2.4701	21.950	2576.1
Liquid, T = 120.00 K					
30.5214	22.898	3907.0	14.5188	22.641	3548.5
28.2808	22.865	3834.9	11.4885	22.588	3439.0
24.8447	22.812	3744.0	8.8079	22.539	3373.0
21.5976	22.760	3720.8	5.8881	22.484	3282.9
18.0318	22.702	3636.4	2.9157	22.427	3198.3
Liquid, T = 110.00 K					
31.0798	23.256	5110.2	14.5234	23.047	4564.3
28.3273	23.223	4962.1	10.9282	22.997	4368.6
24.2702	23.174	4859.8	8.1575	22.958	4294.0
21.4231	23.138	4781.0	5.1533	22.914	4145.0
17.7614	23.091	4690.0	2.3198	22.871	4067.8
Liquid, T = 100.00 K					
30.4263	23.594	7358.7	14.4812	23.444	6209.7
28.2700	23.574	7057.9	11.0224	23.408	6048.3
24.8087	23.543	6885.7	8.1537	23.379	5887.6
21.3234	23.510	6656.6	5.1268	23.347	5729.3
17.9923	23.478	6431.0	2.2322	23.315	5572.9

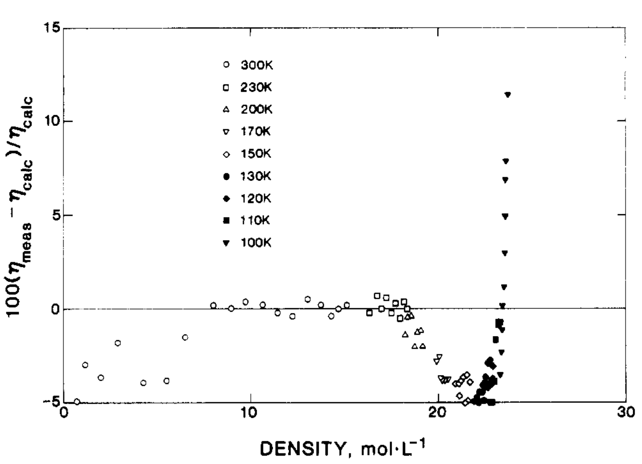

Figure 5. Comparison of viscosity measurements on compressed gaseous and liquid 0.34528 methane + 0.65472 ethane with the extended corresponding states model (*4*, *5*).

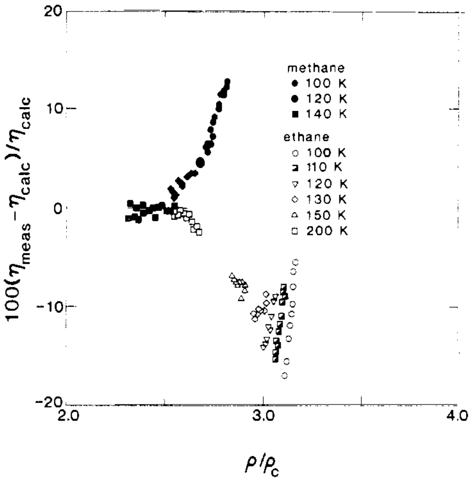

Figure 6. Comparison of viscosity measurements on compressed liquid methane (*2*) and compressed liquid ethane (*3*) with the extended corresponding states model (*4*, *5*).

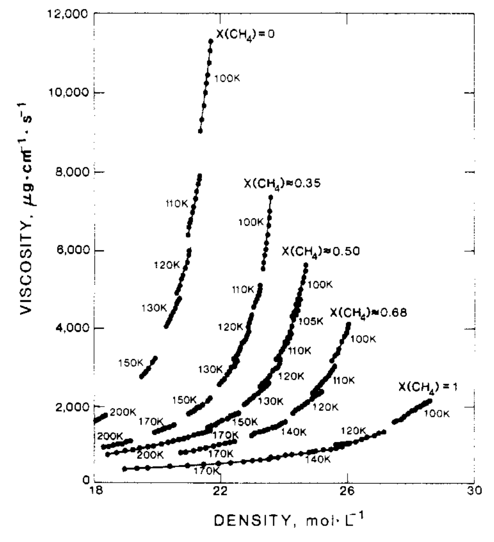

Figure 7. Viscosity of compressed liquid methane + ethane mixtures and their pure components as a function of density with composition and temperature as parameters.

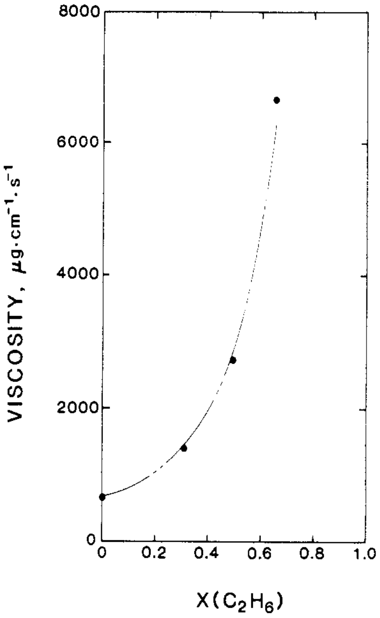

Figure 8. Viscosity of compressed liquid methane + ethane mixtures at fixed density (23.5 mol·L⁻¹) as a function of composition (mole fraction ethane). The temperatures vary with composition and range from 100 to 140 K. Measured viscosities, ●; extended corresponding states model (*4*, *5*), — — — — —.

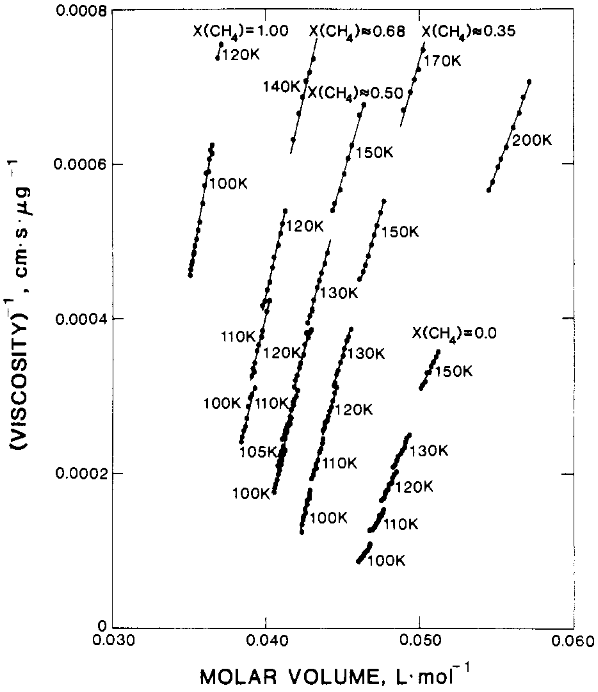

Figure 9. (Viscosity)$^{-1}$ of compressed liquid methane + ethane mixtures and the pure components as a function of molar volume with composition and temperature as parameters.

densities ($\rho > 2\rho_c$), the differences between the measurements and the model range from −5% to +11%. The pattern of the differences obtained for the other two mixture compositions is similar to the pattern shown in Figure 5; the largest differences occur at liquid densities larger than $2\rho_c$. It is interesting to examine the differences between measured viscosities for the pure components (*2*, *3*) and the same model in the high density range. Figure 6 shows that the differences for pure methane increase rapidly with density to about +12%, and the differences for pure ethane increase rapidly with density to about −17%. This figure suggests that the difference pattern obtained

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for the mixture data may be related to the poor correspondence of the viscosities of the pure components at high densities.

Dependences of the Liquid Viscosities on Density and Composition. Measurements of the viscosities of compressed liquid methane + ethane mixtures and the pure components (*2*, *3*) at high densities ($\rho > 2\rho_c$) are shown in Figure 7. There is clearly a strong dependence of the viscosities on density and composition in this density range. The dependence of the viscosities on temperature at fixed composition and at fixed density is relatively small. The dependences on density, composition, and temperature shown here are qualitatively similar to the dependences obtained by Huang, Swift, and Kurata (*13*) for methane + propane mixtures. The dependence of the viscosities of methane + ethane mixtures on composition at fixed density (23.5 mol·L^{-1}) is shown in Figure 8. The viscosity increases very rapidly with increasing ethane concentration in the vicinity of the equimolar composition. Figure 8 also shows that the composition dependence calculated from the extended corresponding states model (*4*, *5*) is very similar to the measured composition dependence at this density.

Dependence of the Fluidities of Liquid Methane + Ethane on Molar Volume. Hildebrand has shown (*14*) that the equation

$$\eta^{-1} = B(V - V_0)/V_0 \qquad (2)$$

where η^{-1} is called the fluidity, V is the molar volume, V_0 is the volume at $\eta^{-1} = 0$, and B is an empirical coefficient, gives a good account of the viscosities of liquids at high densities. Figure 9 shows the dependence of the fluidities of compressed liquid methane + ethane mixtures and the pure components (*2*, *3*) on molar volume at high densities ($\rho > 2\rho_c$). The fluidities increase linearly with volume at fixed composition and at fixed temperature consistent with eq 2. It appears that the Hildebrand equation could be used to develop a simple correlation for the viscosities of compressed liquid mixtures in a limited density range.

Summary

New absolute viscosity measurements have been reported for three compressed gaseous and liquid methane + ethane mixtures throughout a wide range of *PVT* states. The mixture measurements, along with those for the pure components, have been compared with a multiparameter extended corresponding states model, previously proposed for calculating the viscosities of mixtures of nonpolar fluids throughout a wide range of *PVT* states.

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Howard J. M. Hanley encouraged this work and made helpful comments. James F. Ely provided computer programs for processing and analyzing the data.

Registry No. Methane, 74-82-8; ethane, 74-84-0.

Literature Cited

(1) Diller, D. E. *Int. J. Thermophys.* **1982**, *3*, 237.
(2) Diller, D. E. *Physica A (Amsterdam)* **1980**, *104*, 417.
(3) Diller, D. E.; Saber, J. M. *Physica A (Amsterdam)* **1981**, *108*, 143.
(4) Ely, J. F.; Hanley, H. J. M. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 323.
(5) Ely, J. F.; Hanley, H. J. M. *NBS Tech. Note (U.S.)* **1981**, *No. 1039*.
(6) Haynes, W. M. *Physica (Amsterdam)* **1973**, *67*, 440.
(7) Webeler, R. H. W. Ph.D. Thesis, University of Cincinnati, Cincinnati, OH, 1961 (University Microfilms No. 61-5234, Ann Arbor, MI).
(8) Haynes, W. M.; McCarty, R. D.; Holste, J. C.; Eaton, B. E., National Bureau of Standards, Boulder, CO, unpublished data, 1983.
(9) McCarty, R. D. *NBS Tech. Note (U.S.)* **1980**, *No. 1030*.
(10) Haynes, W. M. *Physica A (Amsterdam)* **1977**, *9*, 569.
(11) Abe, Y.; Kestin, J.; Khalifa, H. E.; Wakeham, W. A. *Physica A (Amsterdam)* **1978**, *93*, 155.
(12) Mo, K. C.; Gubbins, K. E. *Mol. Phys.* **1976**, *31*, 825.
(13) Huang, E. T. S.; Swift, G. W.; Kurata, F. *AIChE J.* **1967**, *13*, 846.
(14) Hildebrand, J. H. "Viscosity and Diffusivity"; Wiley: New York, 1977.

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NEW COMPOUNDS

Synthesis and Spectroscopic Studies of 5-Methyl-3-phenyl- and 5-Methyl-3-(*o*-, *m*-, and *p*-tolyl)-1,2,4-oxadiazoles[†]

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Preparation of four 1,2,4-oxadiazoles, 2a–d, from *O*-acetyl derivatives of benzamidoximes, 1a–d, are reported. Two of them, viz., 2b,c, were not encountered in the literature. Spectroscopic studies (IR, UV, and ^{1}H NMR) were carried out to learn more about these molecules. The effect of lanthanide shift reagent, Eu(fod)$_3$, on the chemical shifts of different protons of these compounds was also examined.

In connection with our interest in 3,5-disubstituted 1,2,4-oxadiazoles we recently required 5-methyl-3-phenyl- and 5-methyl-3-(*o*-, *m*-, and *p*-tolyl)-1,2,4-oxadiazoles, **2a–d**. We would now like to report the synthesis and spectroscopic properties of these heterocyclic compounds. Compounds **2b** and **2c** are new.

Results and Discussion

Synthesis of 1,2,4-oxadiazoles, **2a–d**, was achieved either by refluxing *O*-acetyl derivatives of amidoximes, (*1*), **1a–d**, in dry toluene or just by heating them above their melting points for an extended period of time (Scheme I). After completion of the reaction, the desired oxadiazole was purified by column chromatography followed by crystallization or distillation.

Table I shows the ultraviolet data of 1,2,4-oxadiazoles.

The infrared spectra of **2a** and **2b** had ν(C=N) and ν(C=C) of the aromatic ring between 1500 and 1600 cm^{-1}. It was difficult to assign each one correctly. In **2c** and **2d**, C=N

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