Subscripts

i, j	component i, j
$0i$	pure component i (reference-state value)
∞i	infinite diluted component i

Superscripts

E	excess quantity
L	liquid
V	vapor
+	calculated quantity

Operators

Dz	deviation, $z - z^+$
AA(Dz)	absolute average deviation, $(1/n)\sum_i^n \lvert z - z^+\rvert_i$
SIG(Dz)	standard deviation, $[(1/(n-m))\sum_i^n (z - z^+)_i^2]^{0.5}$
RMS(Dz)	root mean square deviation, $[(1/n)\sum_i^n (z - z^+)_i^2]^{0.5}$

Registry No. 1-Chlorohexane, 544-10-5; toluene, 108-88-3; ethylbenzene, 100-41-4; *n*-propylbenzene, 103-65-1.

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Measurements of the Viscosities of Compressed Fluid and Liquid Carbon Dioxide + Ethane Mixtures

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The shear viscosity coefficients of three compressed fluid and liquid carbon dioxide + ethane mixtures have been measured with a torsional piezoelectric crystal viscometer at temperatures between 210 and 320 K and at pressures to about 30 MPa (4350 psi). The experimental error is estimated to be smaller than 3% in most cases. The measurements have been compared with an extended corresponding states model and have been used to examine the dependences of the fluidities (reciprocal viscosities) on molar volume and composition.

Introduction

Mixtures of carbon dioxide with hydrocarbons are of considerable interest for natural gas processing and for enhanced oil recovery research. Carbon dioxide is an unusual molecule as it has a large quadrupole moment, but no dipole moment. Although viscosities have been measured for both pure carbon dioxide (*1*) and pure ethane (*2*), we are not aware of any published viscosity data for their mixtures.

Apparatus and Procedures

The measurement method, apparatus, and procedures are essentially the same as we have used for our work on pure ethane (*2*) and on pure carbon dioxide (*1*). The same torsional piezoelectric quartz crystal of about 5 cm length and 0.5 cm diameter discussed in ref *3* was used for these measurements. Viscosities were derived from measured resonance curve bandwidths by using the equation (*4*)

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

where ρ is the fluid density, M is the mass, S is the surface area of the crystal, f is the resonant frequency, and Δf is the resonance-curve bandwidth of the crystal, measured at one-half of the conductance at resonance. The frequencies, f_{vac} and Δf_{vac}, are measured with the cell evacuated. The difference between f and f_{vac} is usually negligible.

The gas mixture compositions, prepared gravimetrically from research grade carbon dioxide and research grade ethane, are summarized in Table I.

Chromatographic tests on the pure components showed that total impurities were below the 0.01% level for both gases. The errors in the mixture compositions are estimated to be smaller than 0.01%.

Table I. Carbon Dioxide + Ethane Mixture Compositions

mixture	carbon dioxide, mole fraction	ethane, mole fraction
1	0.492 45	0.507 55
2	0.251 66	0.748 34
3	0.739 78	0.260 22

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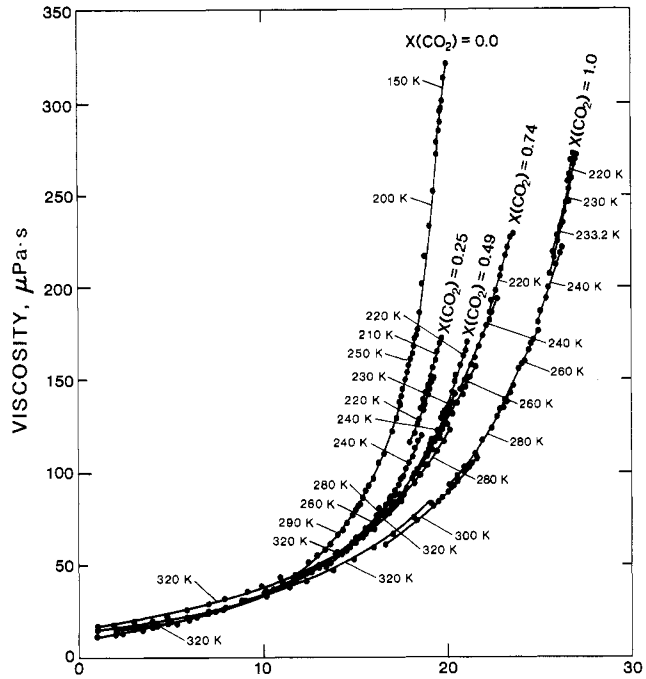

Figure 1. Dependences of the viscosities of compressed fluid and liquid carbon dioxide + ethane mixtures on density. Lines are drawn through the data to guide the eye.

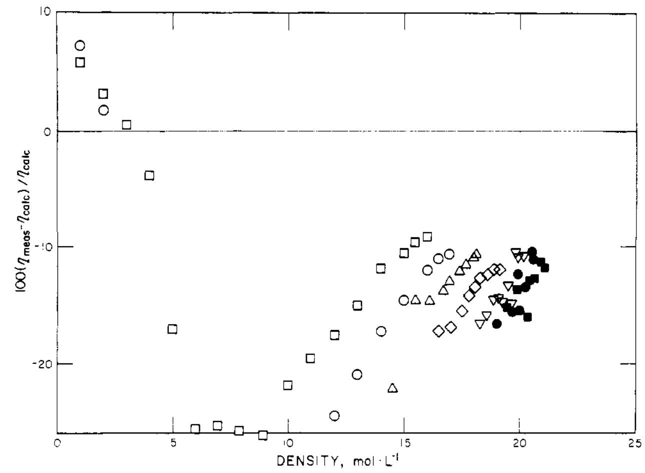

Figure 2. Comparison of the viscosities of 0.492 45 carbon dioxide + 0.507 55 ethane with the extended corresponding states model (14): (□) 320 K; (⊙) 300 K; (△) 280 K; (◇) 260 K; (▽) 240 K; (●) 230 K; (■) 220 K.

Each mixture was heated to a temperature well above its critical temperature and then compressed to a pressure well above its critical pressure before being introduced to the viscometer cell. The critical line for this mixture is given in ref *5*. For measurements on the liquid phase, the cell was cooled while adding fluid to keep the pressure well above the critical

Table II. Viscosities of Compressed Gaseous and Liquid 0.49245 Carbon Dioxide + 0.50755 Ethane Mixtures

T, K	P, MPa	ρ, mol·L^{-1}	η, μPa·s
320.00	34.3873	16.040	74.8
320.00	29.7067	15.535	70.0
320.00	25.5173	14.986	64.8
320.00	19.9742	14.016	57.1
320.00	15.9931	12.972	49.6
320.00	13.5507	11.995	44.0
320.00	11.9284	11.018	39.7
320.00	10.7520	9.973	35.7
320.00	9.9238	8.950	31.2
320.00	9.2246	7.856	27.2
320.00	8.7437	7.016	24.7
320.00	8.1179	5.941	22.0
320.00	7.5228	5.045	19.9
320.00	6.6772	4.016	18.0
320.00	5.6516	3.051	16.6
320.00	4.1933	2.004	15.5
320.00	2.3337	0.987	14.7
300.00	32.4496	16.951	83.3
300.00	27.6136	16.503	78.4
300.00	23.1430	16.003	72.9
300.00	16.5211	14.990	63.2
300.00	12.4114	13.998	55.6
300.00	9.8833	12.984	48.8
300.00	8.4985	12.012	44.1
300.00	7.7570	11.089	39.3
300.00	7.3112	10.116	35.9
300.00	6.9646	8.838	31.0
300.00	6.7513	7.751	26.4
300.00	6.6115	6.993	23.8
300.00	6.4109	6.041	21.3
300.00	6.0521	4.886	18.6
300.00	5.6187	4.006	17.3
300.00	4.8189	2.948	15.8
300.00	3.7121	1.969	15.0
300.00	2.1344	0.982	14.5
280.00	34.6235	18.174	99.4
280.00	31.1698	17.943	96.2
280.00	27.5515	17.675	92.1
280.00	24.2078	17.399	88.1
280.00	20.6909	17.069	83.6
280.00	17.1649	16.681	78.9
280.00	13.6195	16.206	74.0
280.00	9.7018	15.505	66.8
280.00	6.1065	14.468	57.5
260.00	33.5978	19.131	114.7
260.00	31.0881	18.995	112.3
260.00	27.6705	18.799	109.3
260.00	24.2241	18.583	105.3
260.00	20.7994	18.346	101.3
260.00	17.6547	18.105	97.1
260.00	13.8553	17.774	92.1
260.00	10.7428	17.456	86.9
260.00	6.8998	16.977	80.9
260.00	3.8527	16.480	76.5
240.00	34.0660	20.135	138.6
240.00	29.3063	19.929	133.6
240.00	26.9680	19.820	131.9
240.00	24.2718	19.689	123.9
240.00	20.8723	19.513	122.7
240.00	17.5230	19.325	117.1
240.00	13.9706	19.106	113.8
240.00	10.5286	18.871	109.7
240.00	7.3008	18.624	103.8
240.00	3.7059	18.306	98.7
230.00	34.8095	20.640	155.1
230.00	31.3936	20.510	152.5
230.00	27.4881	20.353	143.1
230.00	24.2919	20.216	139.5
230.00	21.0745	20.070	133.1
230.00	17.5062	19.897	134.0
230.00	13.7060	19.697	125.0
230.00	10.3406	19.503	121.4
230.00	6.9050	19.285	118.0
230.00	6.3095	19.245	117.7
230.00	3.7306	19.061	111.7
230.00	3.6024	19.051	113.4
220.00	34.1478	21.085	169.5
220.00	31.0910	20.980	166.4
220.00	27.6143	20.854	162.6
220.00	24.1894	20.724	158.6
220.00	20.7429	20.586	152.6
220.00	17.4025	20.444	148.6
220.00	13.9342	20.287	142.8
220.00	10.2167	20.105	138.5
220.00	6.9275	19.930	134.3
220.00	3.6075	19.738	129.3

Table III. Viscosities of Compressed Gaseous and Liquid 0.25166 Carbon Dioxide + 0.74834 Ethane Mixtures

T, K	P, MPa	ρ, mol·L^{-1}	η, μPa·s
320.00	31.4160	14.798	62.1
320.00	21.1480	13.585	50.9
320.00	15.8320	12.556	45.6
320.00	12.6520	11.567	41.6
320.00	10.5550	10.478	37.3
320.00	8.9381	8.924	30.8
320.00	8.0189	7.393	24.6
320.00	7.5457	6.383	21.5
320.00	7.0875	5.439	19.0
320.00	6.3849	4.265	16.6
320.00	5.8158	3.544	15.1
320.00	4.6195	2.426	13.2
320.00	4.0551	2.012	12.6
320.00	2.3018	0.992	11.9
280.00	34.2437	16.810	86.1
280.00	30.8288	16.607	83.4
280.00	27.8011	16.412	80.5
280.00	24.3318	16.164	76.9
280.00	20.8174	15.881	73.0
280.00	17.4378	15.567	69.2
280.00	14.1208	15.203	65.1
280.00	10.5805	14.718	60.2
280.00	7.6093	14.173	55.5
280.00	4.8838	13.419	49.1
260.00	36.1170	17.742	101.9
260.00	32.1680	17.558	97.7
260.00	28.2900	17.362	94.1
260.00	24.4200	17.148	90.0
260.00	21.0010	16.939	87.1
260.00	17.7040	16.716	83.7
260.00	14.0246	16.434	79.0
260.00	10.5381	16.123	74.1
260.00	7.1869	15.765	70.1
260.00	3.6321	15.277	64.6
240.00	36.2400	18.553	120.1
240.00	31.9460	18.389	117.0
240.00	27.9990	18.227	112.5
240.00	24.0450	18.052	107.7
240.00	21.2010	17.918	104.7
240.00	17.6710	17.738	101.6
240.00	13.8220	17.522	97.1
240.00	10.0560	17.286	93.1
240.00	7.1265	17.079	88.3
240.00	3.5840	16.793	84.4
220.00	35.2215	19.306	151.9
220.00	31.4993	19.187	149.2
220.00	27.7915	19.063	144.9
220.00	24.5276	18.948	141.5
220.00	20.8236	18.810	137.2
220.00	17.2957	18.670	133.6
220.00	13.9084	18.526	128.8
220.00	10.4504	18.368	124.6
220.00	7.1436	18.204	120.7
220.00	3.6211	18.013	115.6
210.00	36.2707	19.724	172.6
210.00	31.0845	19.574	169.8
210.00	27.7296	19.472	165.0
210.00	24.3142	19.363	160.9
210.00	20.7431	19.244	156.1
210.00	17.4136	19.127	151.6
210.00	14.5448	19.020	147.1
210.00	11.3239	18.894	143.0
210.00	7.2295	18.722	138.5
210.00	3.6147	18.556	134.2

pressure of the mixture. All viscosity measurements were performed along isotherms. Care was taken to avoid the liquid–vapor phase boundary to prevent a change in the composition; the cell was not evacuated between runs on a liquid mixture. Instead, the cell temperature was increased after each run, and gas was added to obtain the starting pressure for the next run.

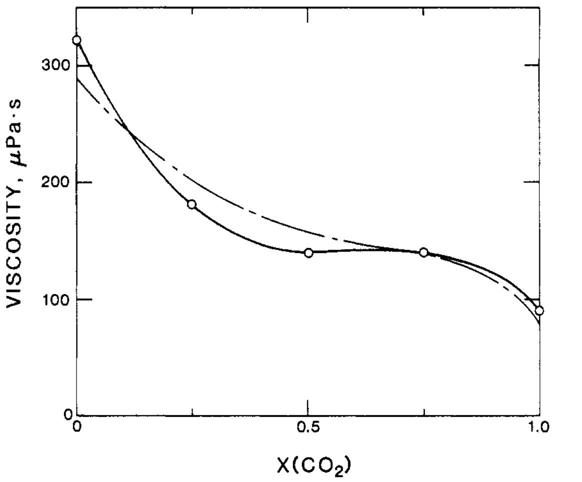

Figure 3. Dependence of the viscosities of compressed liquid carbon dioxide + ethane mixtures on composition at fixed density (20 mol·L^{-1}): (O) interpolated from measurements; (—) curve drawn through interpolated measurements; (- - -) extended corresponding states model (*14*).

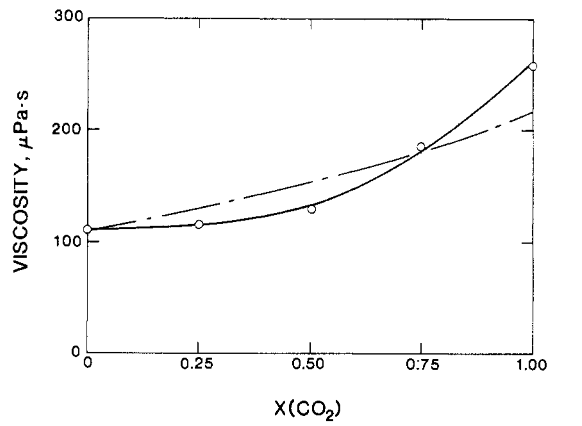

Figure 4. Dependence of the viscosities of compressed liquid carbon dioxide + ethane mixtures on composition at fixed temperature (220 K) and fixed pressure (3.6 MPa): (O) interpolated from measurements; (—) curve drawn through interpolated measurements; (- - -) extended corresponding states model (*14*).

Pressures were measured with a commercial quartz transducer pressure gauge, checked against a commercial piston gauge. The two pressure gauges differed by less than 5 kPa. Densities were obtained from measured temperatures and pressures and a corresponding states equation of state (*6*). The equation of state was compared (*6*) with the measured *PVT* properties of carbon dioxide + ethane mixtures (*7–9*) and is believed to be accurate to better than 1%.

Results and Discussion

Measurements of the viscosities of compressed fluid and liquid carbon dioxide + ethane mixtures are presented in Tables II–IV and Figure 1. The temperature, pressure, and density ranges covered are 210–320 K, 2–30 MPa, and 1–24 mol·L^{-1}, respectively. Measurements were not made in the viscosity critical region, (*5*) which is roughly within 1% of the critical temperature and within 30% of the critical density.

There are no other viscosity data for carbon dioxide + ethane mixtures to our knowledge. Therefore, our estimates of experimental errors are based mainly on comparisons of our pure fluid data with data of others (*3*, *10*, *11*). The differences are generally smaller than 2%. As the densities calculated from ref *6* may be somewhat less accurate than calculated pure fluid densities, we have increased our estimate of the

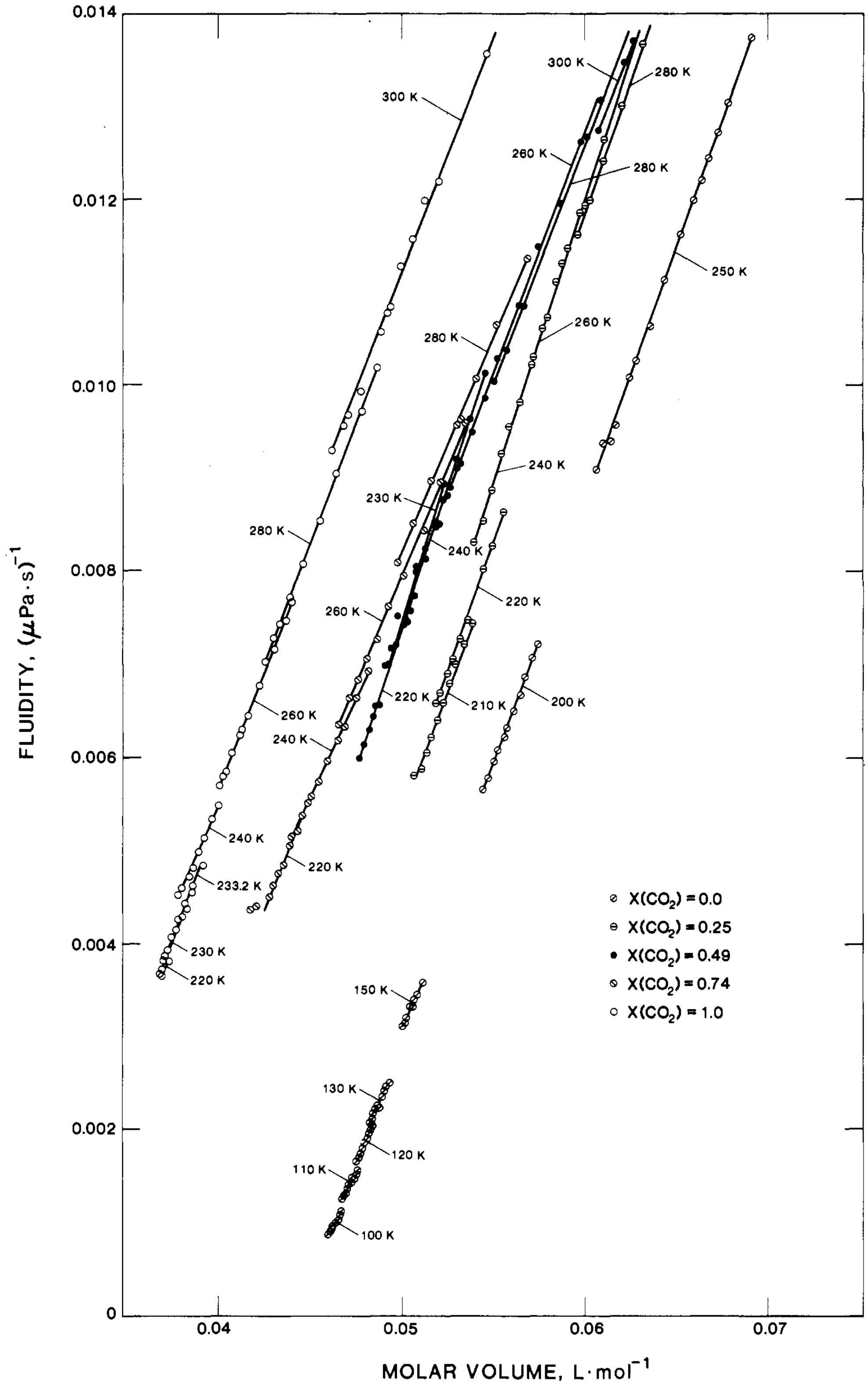

Figure 5. Dependences of the fluidities (reciprocal viscosities) of compressed liquid carbon dioxide + ethane mixtures on molar volume.

viscosity errors to 3%. As the tabulated viscosities were obtained by dividing measured viscosity times density products by calculated densities, they can easily be improved when more accurate densities become available.

The dependences of the viscosities on density and temperature, shown in Figure 1, are similar to the dependences obtained for other pure fluids (*3*, *10*, *11*) and mixtures at fixed composition (*12*, *13*). At high densities the viscosities are strongly dependent on density at fixed temperature and weakly dependent on temperature at fixed density.

The measurements on the nearly equimolar mixture are compared with an extended corresponding states model (*14*) in Figure 2. At densities smaller than 10 mol·L^{-1}, differences up to 25% are caused mainly by density errors contained in the

Table IV. Viscosities of Compressed Gaseous and Liquid 0.73978 Carbon Dioxide + 0.26022 Ethane Mixtures

T, K	P, MPa	ρ, mol·L^{-1}	η, μPa·s
320.00	33.6786	17.523	84.9
320.00	28.1473	16.812	77.7
320.00	23.1584	15.974	69.9
320.00	18.8481	14.966	62.3
320.00	15.7355	13.888	56.4
320.00	13.5679	12.738	52.4
320.00	12.3468	11.779	49.2
320.00	11.5308	10.911	43.4
320.00	10.7960	9.905	39.2
320.00	10.2977	9.086	36.1
320.00	9.6682	7.934	31.7
320.00	9.1354	6.952	28.7
320.00	8.4968	5.899	25.6
320.00	7.6797	4.804	23.1
320.00	6.8785	3.949	21.1
320.00	5.7554	2.990	19.7
320.00	4.1721	1.936	18.4
320.00	2.2809	0.950	18.2
280.00	32.7397	20.068	123.4
280.00	28.6013	19.754	117.4
280.00	24.1290	19.367	111.3
280.00	19.4250	18.884	104.4
280.00	16.3820	18.512	99.2
280.00	13.8850	18.155	93.8
280.00	10.7620	17.608	87.9
280.00	6.4490	16.461	76.2
260.00	35.4640	21.458	157.0
260.00	30.2560	21.168	150.5
260.00	27.2370	20.985	146.2
260.00	24.2100	20.788	141.8
260.00	20.8650	20.551	137.2
260.00	17.4890	20.286	131.3
260.00	13.9040	19.968	125.7
260.00	9.7575	19.536	118.6
260.00	7.1239	19.208	111.7
260.00	3.7949	18.699	104.1
240.00	36.8315	22.666	194.2
240.00	30.5519	22.396	185.8
240.00	27.3746	22.249	181.5
240.00	24.5530	22.111	179.2
240.00	20.7840	21.914	174.1
240.00	17.3490	21.721	167.9
240.00	13.2210	21.467	161.8
240.00	10.5610	21.287	158.1
240.00	6.9454	21.019	150.2
240.00	3.5947	20.737	144.4
220.00	31.5930	23.585	229.4
220.00	27.8190	23.450	227.0
220.00	24.4490	23.323	221.7
220.00	21.0200	23.187	216.5
220.00	21.0968	23.190	216.8
220.00	17.2560	23.030	209.9
220.00	13.9500	22.883	206.3
220.00	10.3790	22.714	198.0
220.00	6.9690	22.542	192.5
220.00	3.6169	22.359	186.0

viscosity model. The viscosity model makes use of a different, and substantially less accurate, equation of state in this range than given in ref *6*. At densities larger than 10 mol·L^{-1} the density errors in the viscosity model are smaller than at low densities, and the differences between measured and calculated viscosities are real deviations from corresponding states. In this density range such deviations are typical for pure fluids (*15*) as well as mixtures (*12*, *13*).

The dependence of the viscosities of liquid mixtures on composition at one fixed density (20.0 mol·L^{-1}) is shown in Figure 3. Our purpose here is to try to examine the dependence on composition alone. It is not possible to fix all of the state variables at once, but work on pure fluids and mixtures at fixed composition has shown that the most important variable to fix at high densities is the density. The composition dependence shown in Figure 3 is somewhat more complicated than the composition dependences obtained for other mixtures we have examined (*12*, *13*). There is an inflection point on the 0.5–0.7 mole fraction carbon dioxide range which may be related to the occurrence of an azeotrope (*16*).

Figure 4 shows the dependence of the viscosities of liquid mixtures on composition at fixed temperature (220 K) and fixed pressure (3.6 MPa). Figure 4 is quite different from Figure 3 since the dependence on composition shown in Figure 4 is combined with the dependence on density and the change in density with composition is substantial at this temperature.

The dependence of the fluidities (reciprocal viscosities) of liquid mixtures on molar volume at fixed compositions and at fixed temperatures is shown in Figure 5. As for pure fluids (*15*), the dependence on volume is linear in this range, which could make possible a relatively simple correlation of these data.

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Registry No. CO_2, 124-38-9; ethane, 74-84-0.

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