Liquid Density of Light Hydrocarbon Mixtures

LeRoy C. Kahre
Research and Development Department, Phillips Petroleum Co., Bartlesville, Okla. 74004

Liquid-density data were obtained for binary systems composed of ethane, propane, butane, and isobutane at 15.6° and 54.4°C and saturation pressure. To validate the mixture densities, data on the pure components were also obtained at several temperatures. The data obtained on pure components agreed with recent literature data normally within ±0.1%. The mixture data showed measurable deviations from ideal mixing (shrinkage) for all systems except butane–isobutane at 15.6°C. The maximum shrinkage observed was about 5% for the ethane–propane system.

There is increasing interest in the petroleum industry in the properties of light hydrocarbon mixtures. Ethane–propane mixtures, available because of more efficient extraction of natural gas, are transported in pipeline quantities. Liquefied petroleum gas (LPG), besides being used as fuel, has a prominent position as an inexpensive aerosol propellant.

In spite of this general interest, little data are available for the volume change on mixing at saturation pressures (shrinkage) of light hydrocarbons. The only published data found for mixtures are the recent values of Tomlinson (*3*) for ethane–propane. The LPG components are normally considered ideal, but apparently, this assumption has not been verified experimentally.

Density data were obtained for ethane–propane, propane–isobutane, propane–*n*-butane, and butane–isobutane at saturation pressure and 15.6°C (60°F) and 54.4°C (130°F) (except for ethane–propane). These temperatures were chosen because 60°F is a standard condition in the petroleum industry, and 54.4°C is a reasonable upper limit for atmospheric conditions. Data on the pure components were also obtained in the interest of validating the mixture densities.

Experimental

Equipment. The experimental equipment (Figure 1) was designed for the measurement of phase-equilibria data and consequently has the advantage of obtaining liquid samples at exactly saturation conditions. No extrapolation (as for isochoric data) or interpolation (as for normal bubble-point data) is required.

The saturated liquid was trapped in sample cylinders, removed by condensing into a weighing cylinder with liquid nitrogen, and weighed on an analytical balance. The sample cylinders were constructed with conical heads to ensure that gas bubbles would not be trapped in them. The volume of the sample cylinders at 15.6°C was determined by calibration with propane, isobutane, and *n*-butane. Using accepted values (*1*) for the densities of these materials, the volumes were calculated from measured weights, and the average volumes were used in future work (Table I). The volume at other temperatures was calculated from the thermal expansion of stainless steel. The expansion of the cylinders with pressure was measured and was negligible.

The cell temperature was measured with a thermocouple and checked against the bath temperature (to better than 0.1°F) which was measured with an ASTM tag thermometer. The cell pressure was measured with a calibrated Heise gage which was exposed to cell liquid for runs above room temperature (to eliminate possible condensation of the vapor phase).

Procedure. *Pure component data.* A sample of Phillips' research-grade hydrocarbon was charged to the evacuated cell, and the bath brought to the desired temperature. A sample of vapor from the cell was obtained and analyzed to assure that the sample was not contaminated with air. The circulating pump was shut off to allow any gas bubbles in the liquid sample cylinders to escape, and the valves of both cylinders were closed. The tared, evacuated, weighing cylinder was attached to the liquid sample line (Figure 1), the connecting lines were evacuated, and the sample from one of the cylinders was condensed into the weighing cylinder with liquid nitrogen. The weighing cylinder was allowed to warm to room temperature, dried thoroughly, and weighed on an analytical balance to ±1 mg. No buoyancy correction was required in the weighings, since the sample was weighed by difference in a stainless-steel container.

The sample in the second cylinder was removed with the same procedure.

Ethane–propane data. After the samples of propane were obtained at 15.6°C, one of the sample cylinders was opened to the cell, and Phillips' research-grade ethane was added to about 10%. The system was equilibrated by recirculating vapor and liquid, and the phases were analyzed by chromatography. The recirculating pump was stopped, the valves of the first sample cylinder were closed, those of the second cylinder opened, and more ethane was added. After the equilibrium liquid from the second run was trapped, both samples were removed from the system and weighed.

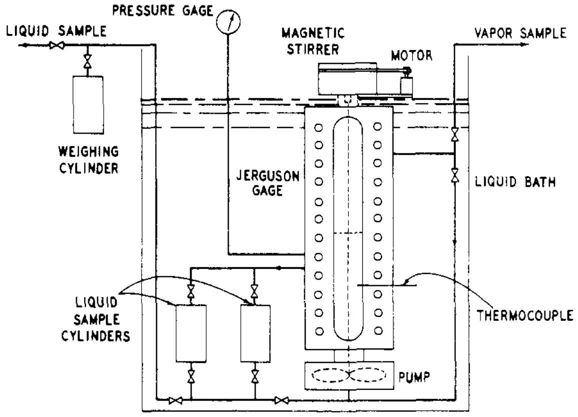

Figure 1. Vapor-liquid equilibrium cell

Table I. Calibration of Sample Cylinders at 15.6°C

Calibrating liquid	Density, g/cm^3 (1)	Volume, cm^3	
		Cylinder 1	Cylinder 2
Propane	0.5072	27.99	27.95
Isobutane	0.5625	28.035	27.98
n-Butane	0.5838	28.06	27.99
Average		28.03	27.97

Table II. Liquid Density of Hydrocarbons at Saturation Pressure

Temperature		Pressure		Density, g/cm^3					
°C	°F	Psia	Atm	Sample 1	Sample 2	Tomlinson	Deviation, %	Sliwinski	Deviation, %
				Ethane					
−5.7	21.8	301.5	20.52	0.4133	0.4133	(0.4141)	−0.19	...	...
4.4	40.0	383	26.06	0.3898	0.3898	0.3896	+0.05	(0.3897)	+0.02
15.6	60.0	492.5	33.51	0.3562	0.3564	0.3563	0.00	0.3557	+0.17
21.1	70.0	556	37.83	0.3354	0.3359	0.3349	+0.22	0.3338	+0.55
26.7	80.0	624	42.46	0.3063	0.3066	0.3058	+0.21	0.3047	+0.57
				Propane					
4.4	40.0	79.5	5.41	0.5225	0.5226	0.5227	−0.03	0.5223	+0.05
15.6	60.0	108	7.35	0.5066	0.5068	0.5069	−0.04	0.5064	+0.06
26.7	80.0	143	9.73	0.4898	0.4900	0.4900	−0.02	0.4896	+0.06
37.8	100.0	188	12.79	0.4716	0.4717	0.4716	+0.01	0.4714	+0.05
54.4	130.0	272	18.51	0.4383	0.4384	(0.4404)	−0.47	0.4402	−0.42
				Isobutane					
4.4	40.0	27	1.84	0.5755	0.5755	...	...	0.5753	+0.04
15.6	60.0	38	2.59	0.5626	0.5627	...	...	0.5621	+0.10
26.7	80.0	52.5	3.57	0.5485	0.5487	...	...	0.5484	+0.04
37.8	100.0	71.5	4.87	0.5345	0.5343	...	...	0.5341	+0.06
54.4	130.0	110	7.48	0.5101	0.5101	...	...	0.5109	−0.16
				n-Butane					
15.6	60.0	26	1.77	0.5844	0.5844	...	...	0.5834	+0.14
54.4	130.0	79	5.38	0.5370	0.5369	...	...	0.5365	+0.08

This procedure was repeated, then ethane was charged to the cell, and propane added incrementally for six more runs.

Propane-butane-isobutane binary data. For these systems the desired mixtures were premixed in relatively large quantities from Phillips' pure-grade hydrocarbons. The particular samples of propane, butane, and isobutane used had purities (as determined by gas chromatography) of 99.8, 99.9, and 99.75%, respectively. It was felt that the small amounts of impurities present would not appreciably affect the mixture densities.

The hydrocarbon mixture was charged to the cell and treated as though it were a pure component (taking the samples for density in duplicate). No analyses were made on these samples, since it was felt that the synthesis would be more accurate than any analyses.

Results

Density data for the pure components are presented in Table II and Figures 2 and 3. The agreement with the recent data of Sliwinski (*2*) and Tomlinson (*3*) is good, in general, better than 0.1%. The greatest deviation is 0.6% for ethane at 26.7°C. The value for ethane listed in the NGPSA data book (*1*) (0.3767 @ 60°F) disagrees considerably (nearly 6%) from any of the recent measurements.

The data for ethane-propane mixtures (Table III) include values for the relative volatilities for ethane to propane. These relative volatility values are included primarily as validation for the measured compositions since they are a sensitive test for the internal consistency of the data (Figure 4).

The liquid-density data for the mixtures at 15.6°C (Tables III and IV) are plotted as a function of composition in Figure 5. The ethane-propane densities agree within about 0.2% with those of Tomlinson. The deviation of these curves from linearity is not a true measure of the shrinkage to be expected in a mixture. Ideal mixing de-

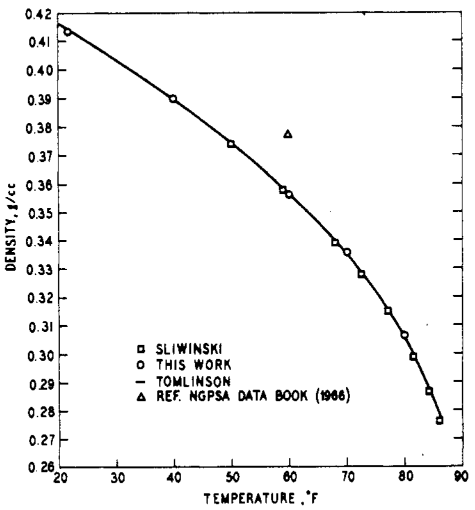

Figure 2. Liquid density of ethane at saturation pressure

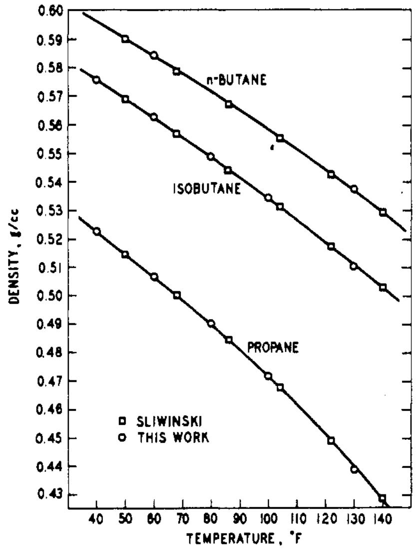

Figure 3. Liquid density of hydrocarbons at saturation pressure

Table III. Liquid Density of Ethane-Propane at 15.6°C (60°F)

Pressure			Composition, mol %				Liquid	Molar vol,	Vol change
Psia	Atm		Liquid	Vapor	$K = y/x$	Relative volatility	density, g/cm^3	cm^3/g mol	on mixing, cm^3/g mol
423.5	28.82	C_2	86.35	93.65	1.084	2.33	0.3897	82.06	−2.69
		C_3	13.65	6.35	0.465				
389	26.47	C_2	78.67	90.09	1.145	2.46	0.4060	81.44	−3.51
		C_3	21.33	9.91	0.465				
342.5	23.31	C_2	68.10	84.63	1.243	2.58	0.4248	81.33	−3.90
		C_3	31.90	15.37	0.482				
319	21.71	C_2	62.09	81.34	1.310	2.66	0.4342	81.51	−3.88
		C_3	37.91	18.66	0.492				
287	19.53	C_2	53.46	76.21	1.426	2.79	0.4470	81.86	−3.75
		C_3	46.54	23.79	0.511				
270	18.37	C_2	48.55	72.90	1.502	2.85	0.4530	82.32	−3.42
		C_3	51.45	27.10	0.527				
239.5	16.30	C_2	40.37	66.59	1.650	2.94	0.4649	82.66	−3.30
		C_3	59.63	33.41	0.560				
206	14.03	C_2	30.94	57.50	1.858	3.02	0.4757	83.56	−2.64
		C_3	69.06	42.50	0.615				
169.5	11.53	C_2	20.03	43.76	2.185	3.11	0.4878	84.62	−1.87
		C_3	79.97	56.24	0.703				
140	9.53	C_2	10.78	27.95	2.593	3.21	0.4983	85.45	−1.28
		C_3	89.22	72.05	0.808				

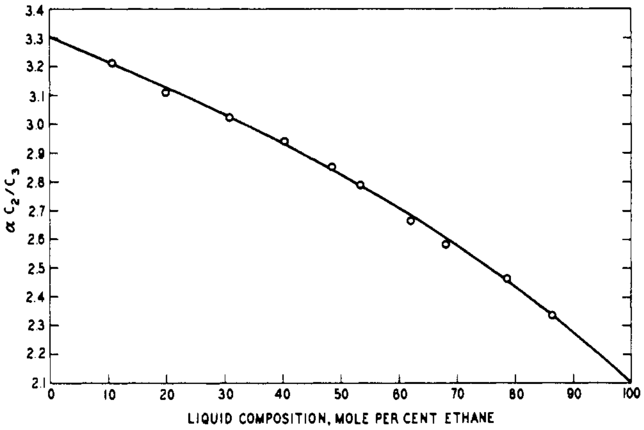

Figure 4. Relative volatility for ethane-propane at 15.6°C

fines a system whose volumes are additive, not whose densities are additive.

A measure of the shrinkage of hydrocarbon mixtures at 15.6°C is presented in Figure 6. The volume change on mixing is calculated as the difference between the actual volume and ideal mixing volume:

$$\Delta V = V_{\text{EXP}} - \Sigma X_i V_i$$

$$V_{\text{EXP}} = \frac{\Sigma X_i M W_i}{\rho}$$

where

ΔV = volume change on mixing, cm^3/g mol
V_{EXP} = experimental molar volume
X_i = mole fraction of component i
V_i = molar volume of component i
MW_i = molecular weight of component i
ρ = experimental liquid density, g/cm^3

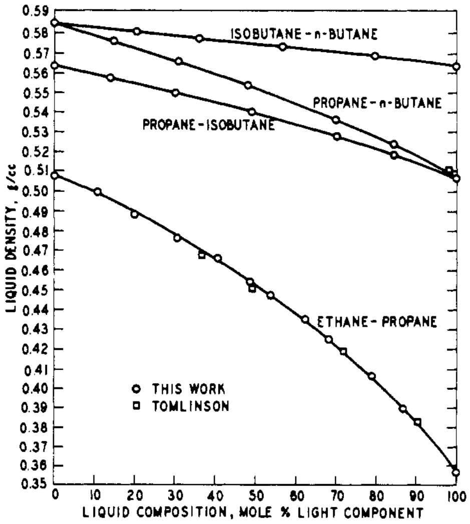

Figure 5. Saturation densities of light hydrocarbon mixtures at 15.6°C

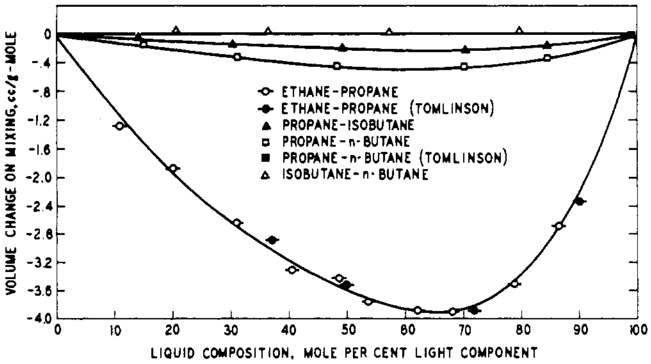

Figure 6. Volume change on mixing at 15.6°C and saturation pressure

Table IV. Liquid Density of Propane–Butane–Isobutane Binaries

Composition light component, mol %	Temperature, 15.6°C (60°F)						Temperature, 54.4°C (130°F)					
	Pressure		Density, g/cm³		Molar vol, cm³/g mol	Vol change on mixing, cm³/g mol	Pressure		Density, g/cm³		Molar vol, cm³/g mol	Vol change on mixing, cm³/g mol
	Psia	Atm	1	2			Psia	Atm	1	2		
						Propane–isobutane						
84.64	96	6.53	0.5176	0.5176	89.35	−0.17	242	16.47	0.4551	0.4552	101.63	−1.00
70.38	85	5.78	0.5267	...	91.61	−0.23	216.5	14.73	0.4668	0.4669	103.36	−1.18
49.32	70	4.76	0.5386	0.5387	95.07	−0.20	182	12.38	0.4822	0.4824	106.18	−1.17
30.21	57.5	3.91	0.5485	0.5485	98.23	−0.15	152	10.34	0.4948	0.4945	108.91	−1.00
14.15	47.5	3.23	0.5561	0.5563	100.93	−0.06	128.5	8.74	0.5039	0.5037	111.43	−0.62
						Propane–*n*-butane						
84.41	93.5	6.36	0.5222	0.5222	88.62	−0.34	236	16.06	0.4611	0.4617	100.30	−1.47
70.07	81	5.51	0.5348	0.5350	90.28	−0.46	205	13.95	0.4775	0.4775	101.13	−1.74
48.30	63	4.29	0.5521	0.5521	93.01	−0.45	163	11.09	0.4990	0.4990	102.91	−1.62
31.11	50	3.40	0.5643	0.5643	95.27	−0.33	131	8.91	0.5140	0.5139	104.59	−1.26
14.87	37.5	2.55	0.5748	0.5748	97.49	−0.14	103.5	7.04	0.5263	0.5262	106.48	−0.61
						Isobutane–*n*-butane						
79.79	36	2.45	0.5667	0.5666	102.56	+0.04	103	7.01	0.5164	0.5165	112.53	−0.25
57.16	33	2.25	0.5716	0.5716	101.68	+0.01	96	6.53	0.5225	0.5225	111.23	−0.27
36.31	31	2.11	0.5759	0.5760	100.90	+0.03	90	6.12	0.5277	0.5278	110.12	−0.18
20.58	28.5	1.94	0.5794	0.5794	100.31	+0.04	85	5.78	0.5316	0.5317	109.31	−0.10

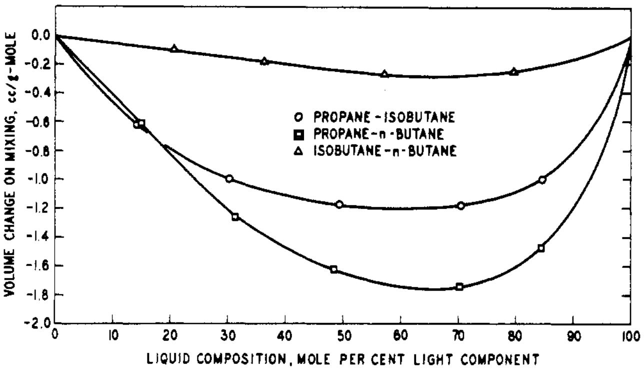

Figure 7. Volume change on mixing at 54.4°C and saturation pressure

The maximum deviation observed at 15.6°C was about 4 cm³/g mol for the ethane-propane system. This represents about 5% shrinkage on mixing or gain in volume on separation (by distillation, for instance). The other systems studied showed much less nonideality. The propane–*n*-butane and propane–isobutane exhibited only 0.5 and 0.2%, respectively. The data actually indicate an expansion on mixing for the butane–isobutane system of about 0.03%, but since this is within experimental error, the system should be considered ideal at 15.6°C.

All the systems studied at 54.4°C (Figure 7) showed greater nonideality than at 15.6°C. Even the butane–isobutane system exhibited measurable shrinkage (about 0.25% maximum) at this temperature.

Literature Cited

(1) "Engineering Data Book," 8th ed., p 154, Natural Gas Processors Suppliers Association, Tulsa, Okla., 1966 (available from Natural Gas Processors Association, 808 Home Federal Building, Tulsa, Okla. 74103).
(2) Sliwinski, P., *Z. Phys. Chem. N.F.*, **63**, 263–79 (1969).
(3) Tomlinson, J. R., Natural Gas Processors Association, Technical Publication TP-1, 1971 (available from NGPA, 808 Home Federal Building, Tulsa, Okla. 74103).

Received for review July 13, 1972. Accepted April 5, 1973.