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Liquid Densities of Propane + Linear Low-Density Polyethylene Systems at (354−378) K and (4.00−7.00) MPa

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Liquid densities have been measured with a variable volume cell for propane + linear low-density polyethylene systems. The temperature and pressure ranges studied are (354−378) K and (4.00−7.00) MPa, and polyethylene mass fractions in the mixtures vary between 0 and 0.0355. Altogether, 107 liquid density data points are reported. The results obtained for pure propane agree well with literature values. Results show that densities increase almost linearly with increasing mass fraction of the polymer.

Introduction

Phase equilibria of polyethylene + hydrocarbon systems has been widely investigated over the past few decades. In some investigations, long-chain alkanes have been used as model components for small polyethylene molecules. However, the liquid densities of the systems are rarely reported. Liquid density is nevertheless a fundamental physical property, thus being interesting in the theoretical sense, and also a property that is often needed in practical engineering calculations and process control.

Earlier phase equilibrium studies on related systems include the papers by Peters et al. (1989, 1992, 1993) on the phase equilibria of propane + long-chain alkane systems and by Condo et al. (1992) on propane + polyethylene systems. Liquid densities on similar mixtures have been previously published by Nieuwoudt (1996), who reported both vapor−liquid equilibria and densities for the system butane + hexacontane, and by Aalto and Liukkonen (1996), who reported density and bubble point pressure measurements in propane + long-chain alkane systems.

In this work, liquid densities for propane + linear low-density polyethylene mixtures have been measured using a variable volume optical cell. The temperature and pressure regions studied are in the vicinity of the critical point of propane. The reported data points are located in the one-phase region, i.e., above the cloud point pressure.

Experimental Section

Materials. The propane used in these measurements was supplied by AGA Oy (purity 99.95 mol %). Linear low-density polyethylene was obtained from Borealis Pilot Plant and subsequently fractionated using propane as the solvent. The fraction that had been dissolved in propane, which had a number average molecular weight M_n of 300 g/mol (weight average molecular weight $M_w = 490$ g/mol), was used in the reported measurements.

Apparatus. Measurements were performed using a DB Robinson Jefri sapphire glass cell apparatus. This apparatus, as well as the procedure, were described in more detail in an earlier paper (Aalto and Liukkonen, 1996). In brief, the glass cylinder is thermostated within an air bath, and the volume of the sample (and therefore pressure as well) can be varied by moving the piston inside the cylinder. The maximum volume of the cylinder is approximately 56 cm^3. Temperature and pressure can be measured with sensors located in the top of the cylinder. Sample volume can be calculated from the cylinder cross-sectional area and the positions of the piston and the upper end of the cylinder, which are determined with a cathetometer. Because the cylinder is transparent, it is possible to see the experimental fluid and make sure the system is in one phase.

Procedure. A known mass of the polymer sample is loaded into the cylinder. The amount of propane added into the cylinder is determined by measuring the volume of the propane in the liquid state (at known temperature T and pressure P). The density of propane at those conditions is estimated from the HBT correlation (Thomson et al., 1982), which is known to be highly accurate. The amount of propane is corrected for the volume taken by the polyethylene sample. This volume is obtained from the known mass of PE and by approximating the PE density with the density of the unfractionated polymer, which is 0.937 g/cm^3 (gradient column). The sample is now heated to the first experimental temperature, and the system is given approximately 1 h time to reach equilibrium. Sample volumes are then measured at all experimental pressures while the temperature is kept constant. The measurements are then continued following the same steps: heating, equilibration time, and determination of sample volumes at experimental pressures.

Accuracy. The uncertainties in the measured temperatures and pressures are ±0.05 K and ±0.001 MPa, respectively. The location of the piston and the upper end of the cylinder can be determined within ±0.001 cm each, which results in ±0.01 cm^3 uncertainty in the volume (typically 30−40 cm^3 at the experimental conditions). The mass of polyethylene is known within ±0.0001 g, while the determined mass of propane has an uncertainty of ±0.010 g. The typical mass of propane used in the measurements is 13−14 g, and the mass of polyethylene is 0.130−0.500 g depending on the intended mass fraction. Consequently, the relative error in the mass fraction of PE becomes ±0.15%. The reported density values should be accurate within ±0.19%.

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Table 1. Measured Densities for Propane (1) + LLDPE (2)

T/K	P/MPa	ρ/(kg·m^{-3})	T/K	P/MPa	ρ/(kg·m^{-3})
$w_2 = 0$					
358.7	3.999	366.5	368.4	4.151	292.1
358.7	5.001	384.1	368.7	4.998	342.6
358.8	5.501	391.0	368.7	5.498	356.1
358.8	5.998	395.6	368.7	5.999	365.1
358.8	6.403	399.7	368.7	6.498	373.7
358.8	7.003	405.6	368.7	7.000	380.5
363.5	4.004	340.3	373.2	4.549	244.2
363.6	4.996	366.7	373.5	4.996	308.7
363.7	5.506	375.9	373.6	5.490	331.7
363.7	6.006	383.1	373.6	5.994	347.3
363.7	6.402	387.8	373.6	6.405	355.2
363.7	7.001	394.0	373.6	7.004	366.1
$w_2 = 0.0094$					
358.5	4.998	388.1	363.5	6.197	387.3
358.6	5.502	395.1	363.5	6.399	389.2
358.6	5.998	399.0	363.5	6.603	392.5
358.6	6.197	400.8	363.6	6.995	395.6
358.6	6.406	402.3	368.3	6.004	369.6
358.6	6.596	404.5	368.4	6.201	372.7
358.6	7.000	407.0	368.4	6.399	375.5
363.5	5.502	378.2	368.4	6.599	378.9
363.5	5.998	384.6	368.4	7.001	382.6
$w_2 = 0.0097$					
353.8	3.999	389.4	373.5	6.198	356.0
353.9	4.994	401.8	373.5	6.399	361.5
353.9	5.498	407.0	373.5	6.603	364.7
353.9	5.998	411.5	373.5	6.998	370.8
353.9	6.200	413.1	378.2	6.202	337.5
353.9	6.400	414.9	378.2	6.400	342.2
353.9	6.603	415.7	378.2	6.600	346.9
353.9	7.004	419.9	378.2	6.999	354.9
$w_2 = 0.0101$					
358.5	4.996	387.7	363.5	6.200	387.4
358.5	5.502	393.7	363.5	6.398	390.1
358.5	5.997	398.4	363.5	6.599	392.2
358.5	6.203	400.6	363.5	6.998	397.0
358.5	6.400	403.3	368.3	5.997	369.4
358.5	6.602	405.0	368.3	6.202	372.8
358.5	7.000	409.0	368.3	6.402	375.9
363.5	5.497	379.2	368.3	6.602	378.1
363.5	6.003	385.4	368.3	6.999	383.7
$w_2 = 0.0232$					
358.7	5.000	393.7	363.7	6.203	394.7
358.7	5.498	400.5	363.7	6.401	396.7
358.7	6.000	404.7	363.7	6.603	399.4
358.7	6.204	407.2	363.7	7.000	403.3
358.7	6.398	409.2	368.6	5.997	377.0
358.7	6.601	411.2	368.6	6.202	379.9
358.8	7.000	414.8	368.6	6.399	382.9
363.7	5.501	385.3	368.6	6.602	385.6
363.7	6.001	392.3	368.6	6.999	389.7
$w_2 = 0.0355$					
358.7	5.001	396.6	368.5	6.001	381.1
358.7	5.500	402.7	368.5	6.199	384.2
358.7	6.001	407.9	368.5	6.399	387.1
358.7	6.202	410.1	368.5	6.600	389.5
358.7	6.401	411.5	368.5	6.997	393.7
358.7	6.601	413.1	368.5	7.097	395.0
358.7	6.999	416.4			

Results and Discussion

The results of the density measurements are shown in Table 1. Measurements were made at temperatures from 354 to 378 K with 5 K intervals. The pressures start at 4.00 MPa and go up to 7.00 MPa. Mass fractions w_2 of the polymer are 0.0, 0.0094, 0.0097, 0.0101, 0.0232, and 0.0355. The results listed are all in the one-phase (liquid or supercritical fluid) region, which is the reason values are not given at lower pressures for all isotherms.

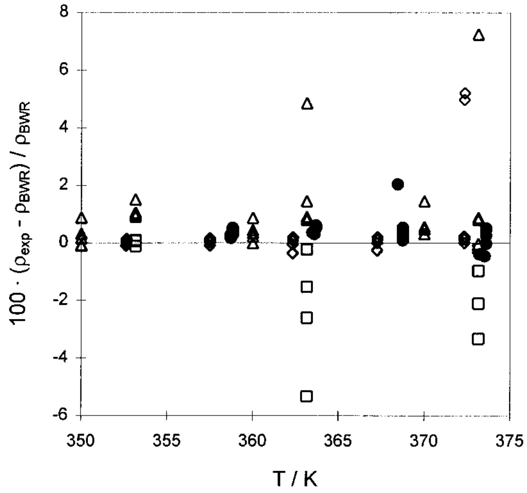

Figure 1. Deviations of measured densities and literature values of pure propane from the BWR-type equation of state by Younglove and Ely (1987). Data sources: ● this work; □ Dittmar et al. (1962); ◇ Defibaugh and Moldover (1997); △ Vargaftik (1975).

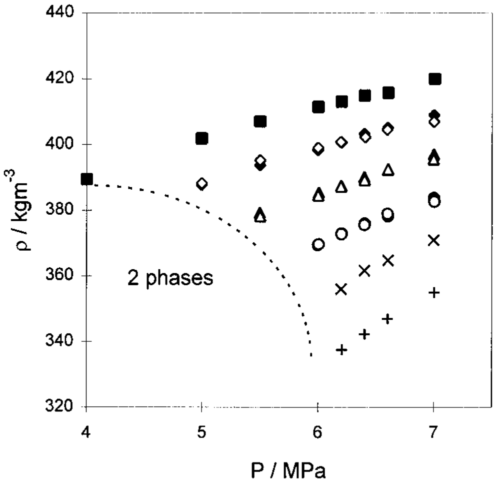

Figure 2. Isotherms obtained for the mixtures where the mass fraction of PE (w_2) is approximately 0.01. The mixture will separate into two liquid phases at low pressures, which is illustrated by sketching the two-phase region boundary. Symbols: ■ 354 K, ◆ 359 K, ◇ 359 K, ▲ 364 K, △ 364 K, ● 368 K, ○ 368 K, × 374 K, + 378 K.

In Figure 1, the measured densities and literature values for pure propane are compared to the BWR-type equation of state by Younglove and Ely (1987), which is based on critically evaluated data, and it is one of the most accurate models available for pure propane. The comparison shows that there is scatter in the literature values, and the results obtained in this work agree well with the BWR equation of state. The average relative deviation between this work and the BWR EOS is 0.45%, which is larger than the accuracy of ±0.19% stated in the previous section. However, according to Younglove and Ely (1987), typical uncertainties in propane densities obtained from the BWR EOS are 0.1% (liquid density below T_c) and 1.5% (critical region), and all the data obtained in this work are at reduced temperatures $T_r \geqslant 0.97$.

Figure 2 shows isotherms obtained for the mixtures where the mass fraction of the polymer (w_2) is approximately 0.01. By looking at the two-phase region in Figure 2, it is clear that the higher the temperature, the higher the pressure has to be in order to keep the mixture in one phase. Phase separation occurs because propane is close to its critical point and propane density decreases

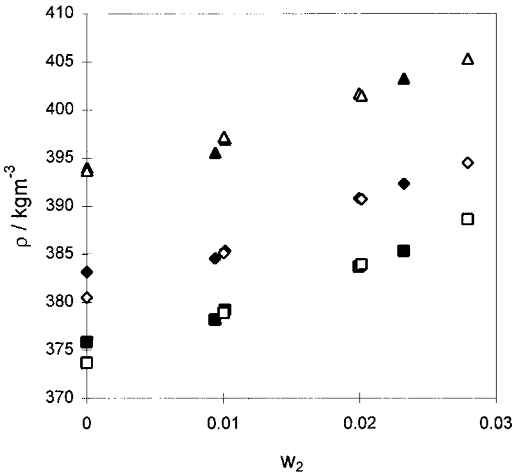

Figure 3. Comparison of this work (black symbols) to earlier results (white symbols) obtained for the propane (1) + pentacontane (2) system (Aalto and Liukkonen, 1996). Three isobars (5.5 MPa, 6.0 MPa, 7.0 MPa) are shown at 364 K. Notations PE and c50 refer to the heavier component in the mixture. Symbols: ■ PE, 5.5 MPa; □ c50, 5.5 MPa; ◆ PE, 6.0 MPa; ◇ c50, 6.0 MPa; ▲ PE, 7.0 MPa; △ c50, 7.0 MPa.

rapidly with increasing temperature (at constant pressure), which results in a substantial increase in the free-volume difference between the components (Folie and Radosz, 1995). In Figure 3, the measured mixture density is shown as a function of w_2, and compared to earlier results on the propane + pentacontane system (Aalto and Liukkonen, 1996). Figure 3 shows that the mixture densities are almost linearly dependent of w_2, and they are not very sensitive to the molecular weight of the heavy component.

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