

Measurement of the densities of complex fluids: results at temperatures between 288 K and 343 K and at pressures up to 30 MPa for each of two mixtures (crude oils) of specified composition

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(Received 15 February 1991)

The densities of two complex mixtures at temperatures between 288 K and 343 K and at pressures up to 30 MPa have been obtained using a direct technique. Both fluids are crude oils, and have bubble pressures greater than 0.6 MPa in our temperature range. Empirical representations are provided for the experimental results.

1. Introduction

In this paper we report densities ρ of two compositionally characterized complex mixtures obtained at temperatures between 288 K and 343 K and at pressures up to 30 MPa using a direct technique.⁽¹⁾ The results have been analysed in terms of the equation:

$$\rho(T, p) = m / \{V_s(T_3, p_3)\} = m / \{V_c(T_3, p_3) - A(T_2, p_2)\rho(\text{Hg}, T_2, p_2) / \rho(\text{Hg}, T_3, p_3) \sum_i \delta l_i\}, \quad (1)$$

where V_s is the volume occupied by the fluid, V_c the cell internal volume, m the mass of sample, A the effective area, and δl the displacement of the positive displacement pump. In equation (1), the subscripts 2 refer to conditions at the positive displacement pump, while those labelled 3 are for temperatures and pressures within the cell.

Empirical representations of the results are provided. In a later paper we shall compare these results, and those reported recently,⁽¹⁾ with standard correlations used in the petroleum industry.⁽²⁾

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2. Experimental

The apparatus and experimental procedures used in this work were identical to those described previously.⁽¹⁾ The samples were provided by BP Exploration.

After completing the measurements for each complex fluid, the sample was separated at known conditions, and the evolved gas and liquid phases were collected. Each of these phases was analysed separately. G.c. analyses were performed using three columns: Poropak Q and 50 nm mean-diameter molecular sieves for the inorganic separation, and a non-polar stationary phase, dimethyl-polysiloxane, for hydrocarbons.⁽³⁾ Liquid hydrocarbon composition was determined using a simulated distillation technique,⁽⁴⁾ for $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ to $\text{CH}_3(\text{CH}_2)_7\text{CH}_3$, and a pseudo-component method for the remainder.⁽⁴⁾ Both used a column packed with dimethyl-polysiloxane. The compositions of the fluids are listed in table 1 after recombination at the conditions recorded during the separation. In these tables the mole fractions given for $\text{CH}_3(\text{CH}_2)_n\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{n+1}\text{CH}_3$ denote all hydrocarbon components eluted immediately after $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ and up to, and including,

TABLE 1. Mole fractions x_i of the i th component in two complex fluids

i	x_i	i	x_i
Fluid no. 1: $\langle M \rangle = 0.15964 \text{ kg} \cdot \text{mol}^{-1}$			
CO_2	0.0017	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3 - \text{CH}_3(\text{CH}_2)_9\text{CH}_3$	0.0420
N_2	0.0010	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	0.0338
CH_4	0.0350	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{11}\text{CH}_3$	0.0353
CH_3CH_3	0.0330	$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	0.0304
$\text{CH}_3\text{CH}_2\text{CH}_3$	0.0639	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$	0.0258
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$	0.0164	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	0.0226
$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	0.0607	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$	0.0215
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	0.0241	$\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$	0.0181
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	0.0440	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{17}\text{CH}_3$	0.0152
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3 - \text{CH}_3(\text{CH}_2)_4\text{CH}_3$	0.0582	$\text{CH}_3(\text{CH}_2)_{17}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$	0.0131
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3 - \text{CH}_3(\text{CH}_2)_5\text{CH}_3$	0.0779	$\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{n>20}\text{CH}_3$	0.1225
$\text{CH}_3(\text{CH}_2)_5\text{CH}_3 - \text{CH}_3(\text{CH}_2)_6\text{CH}_3$	0.0731	C_6H_6	0.0067
$\text{CH}_3(\text{CH}_2)_6\text{CH}_3 - \text{CH}_3(\text{CH}_2)_7\text{CH}_3$	0.0595	$\text{C}_6\text{H}_5\text{CH}_3$	0.0125
$\text{CH}_3(\text{CH}_2)_7\text{CH}_3 - \text{CH}_3(\text{CH}_2)_8\text{CH}_3$	0.0520		
Fluid no. 2: $\langle M \rangle = 0.15923 \text{ kg} \cdot \text{mol}^{-1}$			
H_2O	0.0928	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3 - \text{CH}_3(\text{CH}_2)_8\text{CH}_3$	0.0425
CO_2	0.0014	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3 - \text{CH}_3(\text{CH}_2)_9\text{CH}_3$	0.0354
N_2	0.0001	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	0.0286
CH_4	0.0265	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{11}\text{CH}_3$	0.0313
CH_3CH_3	0.0278	$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	0.0290
$\text{CH}_3\text{CH}_2\text{CH}_3$	0.0711	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$	0.0238
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$	0.0171	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	0.0212
$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	0.0523	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$	0.0216
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	0.0212	$\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$	0.0178
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	0.0323	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{17}\text{CH}_3$	0.0141
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3 - \text{CH}_3(\text{CH}_2)_4\text{CH}_3$	0.0452	$\text{CH}_3(\text{CH}_2)_{17}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$	0.0128
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3 - \text{CH}_3(\text{CH}_2)_5\text{CH}_3$	0.0613	$\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3 - \text{CH}_3(\text{CH}_2)_{n>20}\text{CH}_3$	0.1514
$\text{CH}_3(\text{CH}_2)_5\text{CH}_3 - \text{CH}_3(\text{CH}_2)_6\text{CH}_3$	0.0721	C_6H_6	0.0038
$\text{CH}_3(\text{CH}_2)_6\text{CH}_3 - \text{CH}_3(\text{CH}_2)_7\text{CH}_3$	0.0361	$\text{C}_6\text{H}_5\text{CH}_3$	0.0094

$\text{CH}_3(\text{CH}_2)_{n+1}\text{CH}_3$. The molar mass of the pseudo-component was arbitrarily assigned the value for $\text{CH}_3(\text{CH}_2)_{n+1}\text{CH}_3$. Karl-Fisher titrations were used to determine the mole fraction of H_2O . Only for fluid no. 2 were significant quantities detected. The result is reported in table 1.

Temperatures were measured on IPTS-68 using a long-stem platinum resistance thermometer. Pressures were measured with a precision of 0.01 MPa using a dial gauge (Heise Inc.) which, when calibrated against the oil-lubricated dead-weight tester, was found to be linear to within 0.006 MPa; the gauge was calibrated every second isotherm, and no significant variations were observed. All fluid-head corrections were applied.

3. Results

Densities were measured for fluid no. 1 along four isotherms between 288.15 K and 333.15 K, while for fluid no. 2 five isotherms were studied. The measurement technique, described fully elsewhere,⁽¹⁾ allows determination of ρ with a fractional precision of 0.0002. For the measurements with fluid no. 1 the greatest pressure 30 MPa of the apparatus was used. However, for fluid no. 2 the upper-bound pressure was restricted to 15 MPa. Along all isotherms the lowest pressure was 0.5 MPa. During the course of the 288.15 K isotherm with fluid no. 1 mercury contamination was detected. The apparatus was cleaned and recharged with a new sample before repeating this isotherm.

For all measurements, the volumes of mercury displaced into the cell were corrected for differences between the conditions at the positive displacement meter and those within the cell using the procedure described previously.⁽¹⁾ The corrections were calculated using an expression for the density of mercury given by Moldover *et al.*⁽⁵⁾ In table 2 we list the values of ρ for each of the 39 states investigated for fluid no. 1 above the bubble pressure. The results for fluid no. 2 are also listed in table 2.

4. Analysis and discussion

For fluid no. 1, the mass of mercury injected into the cell was compared twice during the experiment and, in each case, the mass determined by weighing was greater than that calculated from the pump. As with our retrograde-condensate measurements,⁽¹⁾ the laboratory temperature increased during the course of an isotherm, and we suspect that mercury expanded into the cell during the time required to measure the pressure, which could not be accounted for from pump-displacement readings alone. The maximum mass discrepancy of 2 g was detected between the 328.15 K and 313.15 K isotherms and amounts to a fractional uncertainty < 0.0006 in the density. This observed difference was added to the mercury mass expelled from the pump for the subsequent isotherm at 313.15 K. During the 288.15 K isotherm the positive-displacement-pump temperature was invariant. Comparison of the injected mass of mercury with that determined by weighing revealed a small discrepancy of 0.056 g, which would amount to an uncertainty in the volume of 0.004 cm^3 (or about 0.0003

TABLE 2. Densities ρ at temperatures T and pressures p for two complex fluids

T/K	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$
Fluid no. 1						
343.15	1.888	768.778	2.590	769.448	5.044	771.780
	7.579	774.123	10.175	776.461	12.690	778.669
	15.144	780.716	17.599	782.753	20.204	784.818
	25.154	788.629	30.244	792.366		
328.95	1.699	779.668	2.650	780.502	5.175	782.681
	7.710	784.684	10.155	786.912	12.660	788.931
	15.085	791.230	17.750	792.882	20.175	794.686
	25.225	798.314	30.205	801.758		
313.15	1.640	792.341	2.582	793.118	5.177	795.158
	7.642	797.077	10.097	798.976	12.592	800.857
	15.207	802.745	17.712	804.528	20.207	806.227
	25.216	809.570	30.226	812.768		
288.15	2.327	812.633	5.104	814.570	7.649	816.297
	10.195	818.015	12.651	819.634	15.136	821.232
	17.642	822.791	20.117	824.352	22.623	825.864
	25.099	827.394	27.684	828.958	30.190	830.402
Fluid no. 2						
333.15	0.993	789.435	3.155	790.430	4.106	791.263
	5.158	792.152	7.131	793.802	9.115	795.433
	12.120	797.841	15.045	800.105		
323.15	1.592	796.645	2.273	797.207	3.114	797.884
	4.156	798.755	5.148	799.543	7.111	801.082
	9.115	802.656	12.120	804.939	15.135	807.174
313.15	1.322	803.994	2.183	804.672	3.135	805.399
	4.116	806.158	5.138	806.939	7.051	808.376
	9.055	809.842	12.070	812.001	15.125	814.139
301.15	1.251	813.148	2.183	813.840	3.104	814.500
	4.116	815.228	5.108	815.926	7.071	817.299
	9.124	818.737	12.049	820.723	15.025	822.703
288.15	1.071	823.201	2.072	823.908	3.114	824.604
	4.126	825.312	5.138	825.987	7.071	827.261
	9.034	828.527	12.01	830.432	15.045	832.329

of the cell volume occupied by mercury). Clearly, this supports our earlier hypothesis.

The results obtained along each isotherm were used to estimate the bubble pressure p^b which may be represented by

$$p^b/\text{MPa} = 0.91_1 + 1.47_7 \cdot 10^{-3} \{(T/K) - 273.15\}^2, \quad (2)$$

to 0.03_9 .

In the absence of other experimental results with which to compare ours, the internal consistency of our values was checked by comparison with a polynomial smoothing equation. Using the adaptive analysis described previously to select powers of T and p from a bank of terms,^(1,6) the best representation was found to be

$$\begin{aligned} \rho/(\text{kg}\cdot\text{m}^{-3}) = & 823.3_0 - 0.802_9 \{(T/K) - 273.15\} + 0.583_3 (p/\text{MPa}) \\ & + 5.8_6 \cdot 10^{-3} \{(T/K) - 273.15\} (p/\text{MPa}) \\ & - 7.5_0 \cdot 10^{-5} \{(T/K) - 273.15\} (p/\text{MPa})^2, \end{aligned} \quad (3)$$

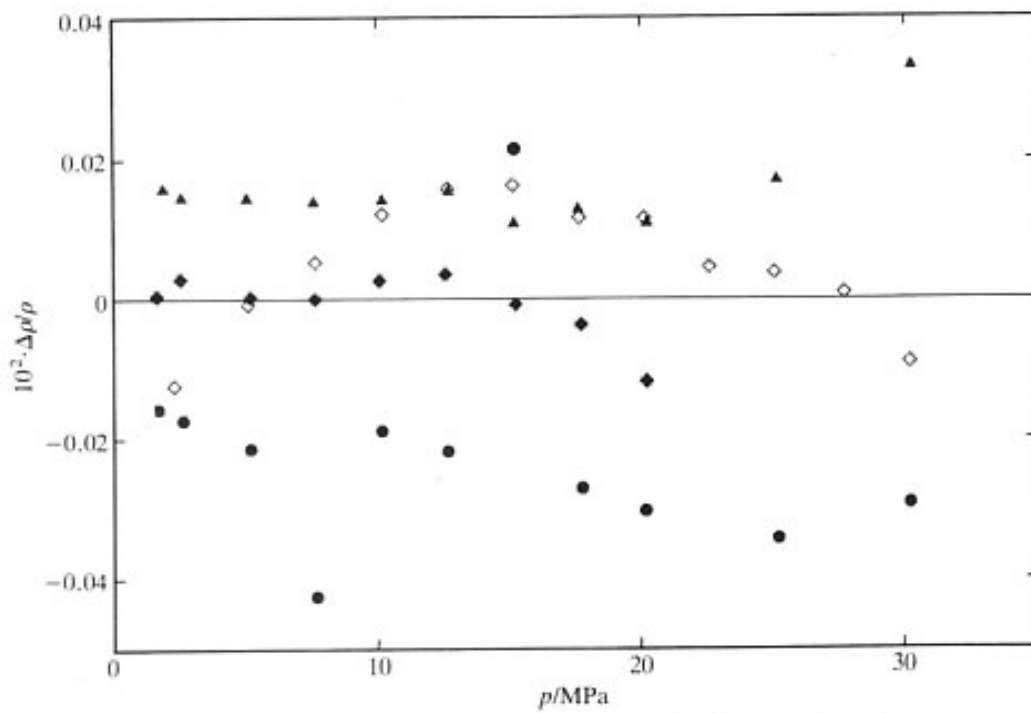


FIGURE 1. Fractional deviations $\Delta\rho/\rho = \{\rho - \rho(\text{calc.})\}/\rho$ of the density of fluid no. 1 from equation (3). \blacktriangle , 343.15 K; \bullet , 328.95 K; \blacklozenge , 313.15 K; \diamond , 288.15 K.

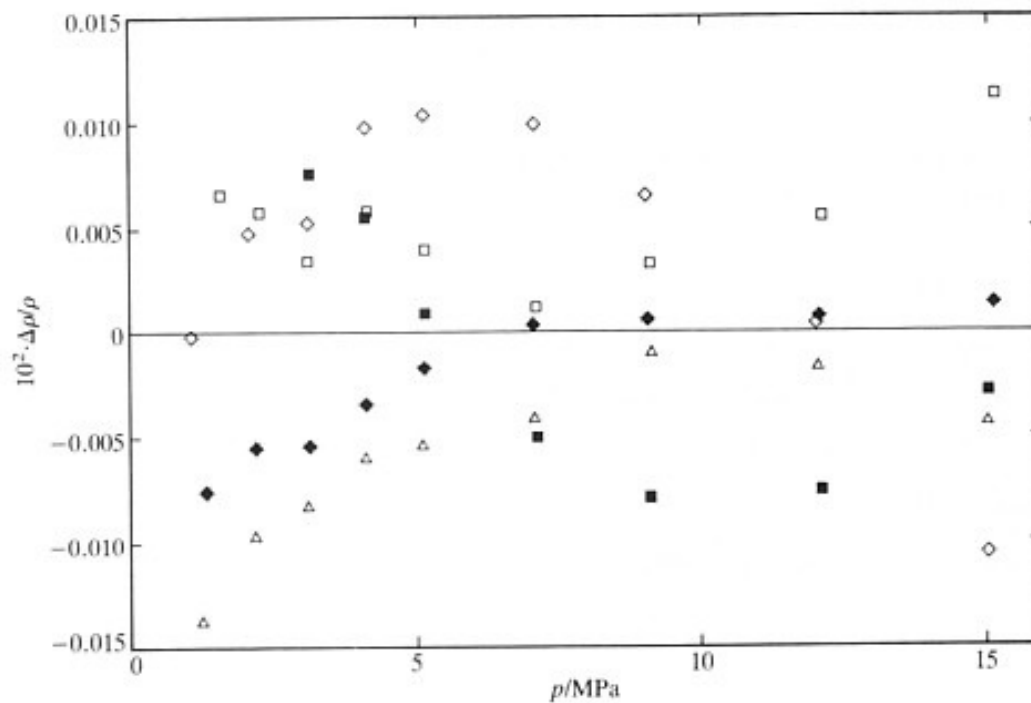


FIGURE 2. Fractional deviations $\Delta\rho/\rho = \{\rho - \rho(\text{calc.})\}/\rho$ of experimental densities for fluid no. 2 from equation (5). \blacksquare , 333.15 K; \square , 323.15 K; \blacklozenge , 313.15 K; \triangle , 301.15 K; \diamond , 288.15 K.

with a standard deviation of 0.1, equal to 0.0003 of the mean value of ρ ; the results are shown as deviations from equation (5) in figure 1. Clearly, the 288.15 K isotherm, which used a second sample charge, is consistent with the other three. We also note that there are inconsistencies in the results which, although small, exceed the imprecision of any one value, and we suspect variations in our mercury inventory are responsible; additional terms in equation (3) did not improve the fit.

During the course of the measurements with fluid no. 2, four comparisons were made between the mass of mercury injected from the positive-displacement pump and that determined by weighing. In each case, the mass determined by weighing was greater than that obtained from pump displacements alone, with a maximum discrepancy equivalent to an uncertainty $0.0003 \cdot \rho$. We again note that these differences could arise from variations in room temperature during the course of an experiment.

From the measurements we were able to estimate the bubble pressure p^b , which could be represented by

$$p^b/\text{MPa} = 0.674_1 + 0.0854\{(T/\text{K}) - 273.15\}, \quad (4)$$

with a standard deviation of 0.009.

The 44 single phase values of $\rho(T, p)$ for fluid no. 2, listed in table 2, are shown in figure 2 as deviations from

$$\begin{aligned} \rho/(\text{kg} \cdot \text{m}^{-3}) = & 834.16_6 - 0.778_4\{(T/\text{K}) - 273.15\} + 0.647_6(p/\text{MPa}) \\ & + 8.1_7 \cdot 10^{-5}(p/\text{MPa})\{(T/\text{K}) - 273.15\}^2 \\ & - 1.8_5 \cdot 10^{-6}[\{(T/\text{K}) - 273.15\}(p/\text{MPa})]^2, \end{aligned} \quad (5)$$

which span $0.00025 \cdot \rho$. The standard deviation of the fit was 0.098; each term entered the regression with a high significance and no other terms remained unselected at the conclusion of the analysis.

We thank BP Research for permission to publish this work and BP Exploration for permission to report the crude-oil measurements.

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