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Pressure Dependence of the Density of *n*-Alkanes

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Accurate density data for *n*-alkanes are essential for the measurement of interfacial tension of liquid–liquid systems as a function of pressure. The variation of density with pressure for three *n*-alkanes, *n*-hexane, *n*-heptane, and *n*-decane, was measured at 21.2°C and pressures ranging from 0.1 to 35 MPa with a digital density meter. The Tait equation of the form $(\rho - \rho_0)/\rho = C \log[(B + P)/(B + P_0)]$ was used to represent the experimental data.

KEY WORDS: alkanes; density; high pressure; interfacial tension; Tait equation.

1. INTRODUCTION

Knowing the functional dependence of interfacial tension, γ, of hydrocarbon–water systems on pressure, P, is important for various reasons. It can be easily seen that the pressure coefficient $(\partial\gamma/\partial P)_T$ (where T is the temperature) has the dimensions of length, and it has been suggested [1, 2] that $(\partial\gamma/\partial P)_T$ is a measure of the thickness of the interface. A knowledge of such γ–P data can also be applied in oil recovery and processing.

The liquid–liquid interfacial tension can be established from the shape of either sessile or pendant drops as described by Cheng et al. [3, 4]. A computer program called Axisymmetric Drop Shape Analysis, or ADSA, was developed to calculate γ by numerically integrating the Laplace equation of capillarity. This equation shows that γ varies directly with the difference between the densities $\Delta\rho$ of the two fluids. A more complete description of ADSA is given by Cheng et al. [3, 4].

The change in interfacial tension of *n*-alkane–water systems with pressure reported by De Filippis [5] and Motomura et al. [2] is only 1 to

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$3\ \mathrm{mJ \cdot m^{-2}}$, in the pressure range of 0.1 to 35 MPa (5000 psi). At the present state of development, ADSA can calculate γ accurately to four significant figures [3, 4]. Thus, in order that $\Delta\rho$ not become the limiting factor in the accurate determination of γ, $\Delta\rho$ must be known to at least as much accuracy. The density of water as a function of pressure is well-known and is tabulated in the literature [6]. But the density of *n*-alkanes is not readily available under these conditions. There are, however, a few sources of accurate *n*-alkane density data in the literature. Dymond and co-workers [7–10] have measured density as a function of pressure for temperatures ranging from 25 to 100°C for several *n*-alkanes. Doolittle [11] has also published P–ρ–T data for several *n*-alkanes at gauge pressures from 0 to 500 MPa and temperatures from 30 to 300°C. All these studies claim an accuracy of better than 0.2%. Better accuracy was obtained in some cases by Dymond et al. [12] when an Anton Paar DMA 512 was used to measure the density as a function of pressure for hexafluorbenzene, hexadeuterobenzene, and benzene at pressures up to 40 MPa, and with an experimental error which can be calculated to be between 0.02 and 0.05%. This same reference also gives the densities of these fluids in the pressure range of 40 to 400 MPa. For this higher-pressure range the experimental procedure used a sealed metal bellows and produced results with an estimated error of between 0.1 and 0.2%. However, there are, typically only a few data points for pressures below 35 MPa (5000 psi). Also, none of these studies measured the density at room temperature (21°C), which is the temperature at which the interfacial tension experiments are being conducted.

Thus, in order to obtain more accurate data, approximately 50 density measurements were made with the Anton Paar density meter (DMA 45), and its external cell (DMA 512), for each of the three *n*-alkanes at 21.2°C in the pressure range 0.1 to 35 MPa. The DMA 512 is capable of measuring densities at pressures between 0 and 40 MPa (6000 psi) and temperatures between −20 and 150°C, with an accuracy of $0.1\ \mathrm{kg \cdot m^{-3}}$ [13].

2. METHODS AND APPARATUS

2.1. Fluids

The *n*-alkanes used were *n*-hexane (C_6H_{14}) with a purity of 99.2%, *n*-heptane (C_7H_{16}), 99.8% pure, and *n*-decane ($C_{10}H_{22}$), 99.6% pure. All three were obtained from the Aldrich Chemical Company. The purity was determined by gas chromatography and reported by De Filippis [5]. The density meter was calibrated with water and nitrogen. The water used was doubly distilled (ultrapure water which has been deionized) with the

Sybron Barnstead NANOpure II still and then degassed by placing it in a desiccator under vacuum for several hours until no more gas bubbles formed. Nitrogen, 99.997% pure, in a 42-MPa (6000-psig) cylinder from Linde Union Carbide was also used. Density as a function of pressure for water and nitrogen is given in Refs. 6 and 14, respectively.

2.2. Experimental Procedure

2.2.1. Density Meter Theory

The density meter works on the principle that the period of oscillation τ (which the density meter measures), of a vibrating U-tube depends on the density of the sample contained in the U-tube. An equation can be written relating the period of oscillation to the density of the sample and the volume, mass, and spring constant of the U-tube. Rearranging this equation and grouping the terms which are constants produce a formula which relates ρ to τ and two constants, A and B. Therefore, if the densities of two substances are known, and the τ values measured, the equation can be solved for the calibration constants A and B using Eqs. (1) and (2).

$$A = \frac{\tau_1^2 - \tau_2^2}{\rho_1 - \rho_2} \tag{1}$$

$$B = \tau_1^2 - A\rho_1 \tag{2}$$

where 1 represents water and 2 nitrogen. These constants will be valid under the conditions of temperature and pressure for which the calibration procedure was conducted. Knowing A and B, the density of any fluid under these given conditions can be found by Eq. (3), where τ is the measured period of oscillation of the fluid [13, 15, 16].

$$\rho = \frac{\tau^2 - B}{A} \tag{3}$$

2.2.2. Density Apparatus

Figure 1 is a schematic of the experimental setup used for the density measurement of the *n*-alkanes. In the calibration procedure there are two modifications of the setup as diagrammed. The first is that the intermediate cell is not used, thus line 10 connects directly to the density meter. The second modification is relevant for the nitrogen run only; during this run the pump is replaced by the nitrogen bottle. Because it is not desirable for the pump (Eldex AA-100-S) to be used to pump hydrocarbons (since the pump would have to be cleaned after each use), an intermediate cell (which

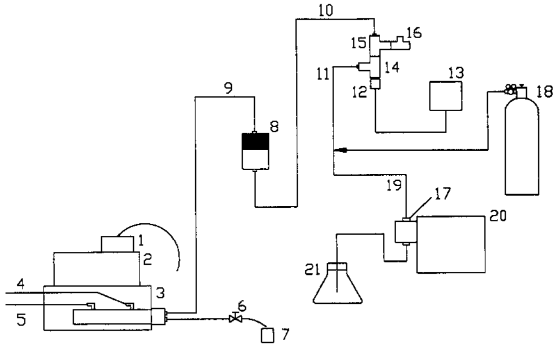

Fig. 1. The density experiment apparatus. (1) Thermocouple. (2) DMA 45. (3) DMA 512. (4) From water bath. (5) To water bath. (6) Discharge valve. (7) Beaker for the discharge. (8) Intermediate cell filled with alkane. (9) Line 2. (10) Line 3. (11) Line 1. (12) Pressure transducer. (13) Display for pressure transducer. (14) Street tee. (15) Tee. (16) Relief valve. (17) Pressure connector. (18) Nitrogen bottle. (19) 316 stainless steel pressure tubing. (20) Pump. (21) Flask of doubly distilled water.

can be readily cleaned) is used. The hydrocarbons are less dense than water and also insoluble. Thus, they float on top of the water, and when the pump is run, the water acts like a piston which pushes the hydrocarbon into the density meter. The fittings used to withstand these pressures are made of stainless steel and were either self-sealing (Swagelok) or wrapped with Teflon tape (Cajon). A Schaevitz number P1021-0005 pressure transducer, which is accurate to ±5 psi (0.03 MPa), was used with an Aries Instruments type 8142-000-00 indicator. A "J" thermocouple was used with an indicator made by Thermo Electric, Model 3164101111, which has a digital readout good to ±0.1°C. The water bath was a MGW Lauda C 12 model B-1.

2.2.3. Experimental Procedure

The temperature of the density meter was controlled by a water bath. The thermocouple was inserted into the density meter before the experiment, to find the proper setting for the water bath. The thermocouple was later placed in the water bath to monitor its temperature. The *n*-alkane experiments are basically the same as the calibration experiments (done with water and nitrogen), except for the differences already mentioned. The system is set up as in Fig. 1, and the density meter is allowed to come to thermal equilibrium with the water bath. The τ value is then recorded and the pressure is increased. The density meter is again allowed time to reach thermal equilibrium (which is indicated by τ coming to a steady value) before τ is recorded. The pressure is again increased, the fluid allowed to come to equilibrium, and τ recorded. This procedure is then repeated until the maximum pressure has been reached. The pressure is then released, and the U-tube cleaned with an appropriate solvent; acetone was used, and the U-tube dried with air using the built-in pump.

3. RESULTS AND DISCUSSION

The experimental results are given in Fig. 2 and in Table I. Fifty data points (represented by the points in Fig. 2) were obtained for each of the three *n*-alkanes. The Tait equation, of the form given by Eq. (4) was chosen to fit the data and is represented by the curve drawn in Fig. 2.

$$\frac{\rho - \rho_0}{\rho} = C \log\left(\frac{B + P}{B + P_0}\right) \tag{4}$$

This equation has been frequently used to fit P–ρ data for compressed liquids and is known to reproduce reliably density data at high pressures [17]. Dymond and Malhotra found that this equation was an excellent

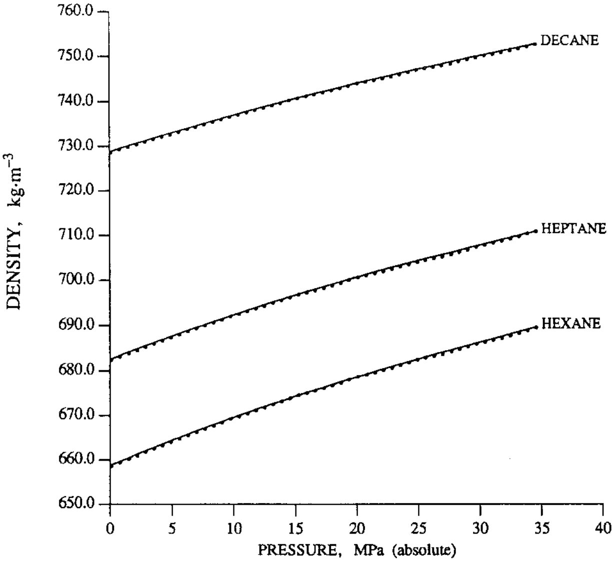

Fig. 2. Density ($kg \cdot m^{-3}$) versus pressure (MPa absolute) for *n*-hexane (99.2%), *n*-heptane (99.8%), and *n*-decane (99.6%) at 21.2°C. The data are represented by the Tait equation.

Table I. Pressure–Density Data for *n*-Hexane, *n*-Heptane, and *n*-Decane

Pressure		Density ($kg \cdot m^{-3}$)		
(psig)	(MPa)	Hexane	Heptane	Decane
0	0.10	658.92	682.68	728.91
100	0.79	659.70	683.41	729.48
200	1.48	660.47	684.12	730.05
300	2.17	661.24	684.83	730.62
400	2.86	662.00	685.53	731.19
500	3.55	662.76	686.23	731.75
600	4.24	663.51	686.92	732.31
700	4.93	664.26	687.60	732.87
800	5.62	665.00	688.28	733.43
900	6.31	665.74	688.95	733.98
1000	7.00	666.48	689.63	734.54
1100	7.69	667.20	690.29	735.09
1200	8.38	667.93	690.94	735.64
1300	9.07	668.65	691.59	736.18
1400	9.75	669.36	692.24	736.72
1500	10.44	670.00	692.82	737.20
1600	11.13	670.62	693.38	737.68
1700	11.82	671.26	693.96	738.17
1800	12.51	671.93	694.56	738.68
1900	13.20	672.60	695.16	739.19
2000	13.89	673.30	695.80	739.73
2100	14.58	674.02	696.45	740.30
2200	15.27	674.67	697.04	740.80
2300	15.96	675.20	697.50	741.20
2400	16.65	675.74	698.00	741.62
2500	17.34	676.32	698.51	742.06
2600	18.03	676.92	699.05	742.53
2700	18.72	677.55	699.63	743.03
2800	19.41	678.22	700.23	743.55
2900	20.10	678.87	700.83	744.06
3000	20.79	679.31	701.22	744.40
3100	21.48	679.78	701.65	744.77
3200	22.16	680.28	702.10	745.16
3300	22.85	680.82	702.60	745.59
3400	23.54	681.40	703.12	746.05
3500	24.23	682.01	703.69	746.53
3600	24.92	682.66	704.29	747.05
3700	25.61	683.09	704.68	747.38
3800	26.30	683.51	705.07	747.72
3900	26.99	683.98	705.50	748.09
4000	27.68	684.48	705.98	748.49
4100	28.37	685.03	706.49	748.93
4200	29.06	685.61	707.04	749.40
4300	29.75	686.23	707.63	749.90
4400	30.44	686.71	708.08	750.28
4500	31.13	687.12	708.48	750.61
4600	31.82	687.57	708.91	750.97
4700	32.51	688.05	709.38	751.36
4800	33.20	688.58	709.89	751.79
4900	33.89	689.14	710.44	752.25
5000	34.58	689.75	711.03	752.74

means of representing P–ρ data [18]. This form of the Tait equation (with log to the base 10) relates density ρ at pressure P to the density (ρ_0) at atmospheric pressure P_0 and the parameters B and C. Equation (4) was fit to the data for each *n*-alkane, and B and C were optimized by the following method. First, the Tait equation was transformed, by using Eqs. (5) and (6), into the linear form of Eq. (7).

$$y = \frac{\rho - \rho_0}{\rho} \tag{5}$$

$$x = \log\left(\frac{B+P}{B+P_0}\right) \tag{6}$$

$$y = Cx \tag{7}$$

An initial value for B was then arbitrarily chosen (for example, $B = 0$), the x values were calculated, and linear regression was used to find C. A new value was then chosen for B and the process repeated until a B value was found which produced the best linear fit. The B and C values are given in Table II and a comparison between the data and the equation is made.

Dymond and Malhotra [18] note that C has sometimes been taken to be independent of temperature and constant for a series of compounds by others; Dymond and Malhotra [18] show that this approximation is valid for their data as well. Table III shows the values for B and C, if C is taken to be constant independent of the *n*-alkanes (these values are denoted B' and C'). The maximum deviation and the standard deviation between the B' and the C' representation and the data are also given. These deviations are fairly small, indicating that the above assumption can also be used to represent our data.

The error in the pressure and temperature measurements are ±0.03 MPa (±0.1%) and ±0.1 K, respectively. The experimental error in ρ has been estimated to be 0.02%, which is approximately the same as Dymond et al. [12] found when they used an Anton Paar density meter.

Table II. Parameters for the Tait Equation[a]

n-Alkane	B (MPa)	C	ρ_0 ($\mathrm{kg \cdot m^{-3}}$)	σ ($\mathrm{kg \cdot m^{-3}}$)	Max. dev. ($\mathrm{kg \cdot m^{-3}}$)
Hexane	40.065	0.1655	658.9	0.097	0.26
Heptane	40.745	0.1484	682.7	0.094	0.17
Decane	52.735	0.1444	728.9	0.071	0.19

[a] Where $\sigma = [(1/n)\sum_1^n(\rho_{\mathrm{expt}} - \rho_{\mathrm{calc}})^2]^{1/2}$ and maximum deviation $= |\rho_{\mathrm{expt}} - \rho_{\mathrm{calc}}|$.

Table III. Parameters for the Tait Equation When C Is Constant

n-Alkane	B' (MPa)	C'	ρ_0 ($kg \cdot m^{-3}$)	σ ($kg \cdot m^{-3}$)	Max. dev. ($kg \cdot m^{-3}$)
Hexane	35.856	0.1528	658.9	0.16	0.29
Heptane	42.388	0.1528	682.7	0.10	0.22
Decane	56.687	0.1528	728.9	0.11	0.27

Table IV shows the constants ρ_0, B, and C, which were calculated from Dymond et al. [10, 18] in order to compare our data with literature values. How these three constants were calculated from the literature is described below. The ρ_0 values for the n-alkanes were obtained by linear interpolation from the following references: n-hexane [7], n-heptane [10, 11], and n-decane [9]. For n-hexane the ρ_0 of this work ($658.9\ kg \cdot m^{-3}$) can also be compared to that of Dymond et al. [8, 20], 658.7 and $658.6\ kg \cdot m^{-3}$, respectively. In the case of n-decane the temperatures were 298.31 and 348.14 K; this was the broadest range of interpolation and may account for the larger discrepancy between the ρ_0 of this work and the interpolated ρ_0. B and C were found for n-heptane by using a linear interpolation over temperature from Ref. 10. Dymond and Malhotra [18] used Eqs. (8) and (9) to calculate B (MPa), where T_R is the reduced temperature given by Eq. (10) and C_n is the number of carbon atoms in the molecule.

$$B_c = 341.537 - 734.292 T_R + 411.189 T_R^2 \tag{8}$$

$$B_c = B + (C_n - 6) \tag{9}$$

$$T_R = \frac{T}{T_c} \tag{10}$$

No critical temperature (T_c) values were given in Ref. 18. Thus, Eq. (10) taken from Tsonopoulos [19] was used to calculate T_c instead:

$$\ln(959.98 - T_c) = 6.81536 - 0.211145 C_n^{2/3} \tag{11}$$

Table IV. Literature Values of the Tait Parameters for n-Alkanes

n-Alkane	B (MPa)	C	ρ_0 ($kg \cdot m^{-3}$)	T_c (K)	σ ($kg \cdot m^{-3}$)	Max. dev. ($kg \cdot m^{-3}$)
Hexane [17]	53.592	0.2000	658.9	505.94	0.92	1.11
Heptane [17]	62.231	0.2000	682.8	538.95	0.81	1.00
Heptane [10]	67.896	0.213	683.0	—	0.81	0.99
Decane [17]	80.648	0.2000	729.4	623.64	0.18	0.50

Since the T_c used in this work may not be identical to the value used by Dymond and Malhotra [18], some discrepancies could be introduced into B. However, these discrepancies should be fairly small since the difference between the T_c used by Dymond and Malhotra [18] and the T_c used in this work cannot be very large. Table IV also lists the standard and maximum deviations between the studies of Dymond et al. [10, 18] and the present work using B and C. A comparison between this work using B' and C' and the studies of Dymond et al. [10, 18] shows similar deviations. (Note that this comparison is not presented in Table IV.) The deviations in the representations of P–ρ data between this work and the literature values could be attributed to the larger error (0.02 vs 0.2%), the lower number of points on an isotherm (50 vs 10), and the larger pressure range (35 vs 500 MPa) used by others. Small deviations in the Tait equation of best fit used at lower pressures will not lead to significant differences. This work used a pressure range of 0.1 to 35 MPa, which is more limited than the pressure range used by others. The Tait parameters of this work and Dymond et al. [10, 18] are not exactly the same; these discrepancies may be due to the fact that Dymond et al. [10, 18] optimized the Tait equation over a broader range than is used in the present study.

4. CONCLUSIONS

Accurate values for the pressure dependence of the density of *n*-hexane, *n*-heptane, and *n*-decane are presented at 21.2°C from 0.1 to 35 MPa can be well represented by the Tait equations developed in this paper. The experimental error in the P–ρ data has been estimated to be 0.02%. The Tait parameters for each of the *n*-alkanes were optimized by using 50 data points on the 21.2°C isotherm. It should also be noted that the parameter C can be assumed constant for all three of these *n*-alkanes.

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REFERENCES

1. R. J. Good, *J. Colloid Interface Sci.* **85**:141 (1982).
2. K. Motomura, H. Iyota, M. Aratono, M. Yamanaka, and R. Matuura, *J. Colloid Interface Sci.* **93**:264 (1983).
3. P. Cheng, *Automation of Axisymmetric Drop Shape Analysis Using Digital Image Processing*, Ph.D. thesis (University of Toronto, Mech. Eng., Toronto, Canada, 1990).

4. P. Cheng, D. Li, L. Boruvka, Y. Rotenberg, and A. W. Neumann, *J. Colloids Surfaces* **43**:151 (1989).
5. F. De Filippis, *The Pressure and Temperature Dependence of the Interfacial Tension of Hydrocarbon-Water Systems Using Axisymmetric Drop Shape Analysis*, M.A.Sc. thesis (University of Toronto, Mech. Eng., Toronto, Canada, 1989).
6. L. Haar, J. S. Gallagher, and G. S. Kell, *NBS/NRC Steam Tables* (Hemisphere, New York, 1984).
7. J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.* **1**:345 (1980).
8. J. H. Dymond, K. J. Young, and J. D. Isdale, *J. Chem. Thermodyn.* **11**:887 (1979).
9. J. H. Dymond, J. Robertson, and J. D. Isdale, *J. Chem. Thermodyn.* **14**:51 (1982).
10. J. H. Dymond, R. Malhotra, J. D. Isdale, and N. F. Glen, *J. Chem. Thermodyn.* **20**:603 (1988).
11. A. K. Doolittle, *J. Chem. Eng. Data* **9**:275 (1964).
12. J. H. Dymond, N. Glen, J. Robertson, and J. D. Isdale, *J. Chem. Thermodyn.* **14**:1149 (1982).
13. *Instruction Manual External Measuring Cell, DMA* (Anton Paar, Graz, Austria).
14. B. A. Younglove, *Thermophysical Properties of Fluids 1. Argon, Ethylene, Parahydrogen, Nitrogen, Nitrogentetrafluoride, and Oxygen* (J. Phys. Chem. Ref. Data 11, American Chemical Society and American Institute of Physics, 1982).
15. O. Kratky, H. Leopold, and H. Stabinger, *Calculating Digital Density Meter for Liquids and Gases Instruction Manual, DMA 45* (Anton Paar, Graz, Austria).
16. *Density and Related Values, DMA* (Anton Paar, Graz, Austria).
17. J. H. Dymond and R. Malhotra, *Int. J. Thermophys.* **9**:941 (1988).
18. J. H. Dymond and R. Malhotra, *Int. J. Thermophys.* **8**:541 (1987).
19. C. Tsonopoulos, *AIChE J.* **33**:2080 (1987).
20. J. H. Dymond and K. J. Young, *Int. J. Thermophys.* **1**:331 (1980).