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An Improved Representation for *n*-Alkane Liquid Densities

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New experimental density data have been used to improve a recently published correlation of *n*-alkane densities, based on the Tait equation. The new correlation covers the *n*-alkanes from methane to *n*-hexadecane in an extended pressure range of up to 500 MPa in some cases. The overall average deviation of the experimental measurements of the density from those calculated by the correlation is ±0.10%. A simple extension to *n*-alkane mixtures gives a satisfactory prediction of the density compared with experimental data.

KEY WORDS: *n*-alkanes; density; high pressure; Tait equation.

1. INTRODUCTION

In a series of recent papers [1–5] it has been shown that for the correlation of transport properties of liquids over a wide temperature range and up to elevated pressures, it is the density which is the important parameter. In the specific case of *n*-alkanes, a scheme based on consideration of the hard-sphere theory [1, 3, 4] enabled the correlation and prediction of the transport properties of the pure components and their mixtures, as a function of their density, in the temperature range 100–400 K and up to 500 MPa, to be made with an uncertainty of about 5%. For such purposes, the densities must be known with an uncertainty better than 0.2%.

The application of the Tait equation as a means of correlating the density of the *n*-alkanes was examined by Dymond and Malhotra [6]. However, recent accurate density measurements on *n*-pentane up to elevated pressures [7] show an average deviation of 0.35% from values

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given by the correlation. In this paper, an improved representation of n-alkane liquid density is reported for all n-alkanes from methane to n-hexadecane, taking into account the n-pentane results and other more recent experimental density measurements which extend the temperature and pressure range.

2. THE CORRELATION

The Tait equation is usually expressed in the form

$$\frac{\rho - \rho_0}{\rho} = C \log \left[\frac{B + P}{B + P_0} \right] \tag{1}$$

where ρ and ρ_0 are the liquid densities at the correponding pressures, P and P_0, and B and C are parameters. In most cases P_0 is taken equal to the atmospheric pressure (0.101 MPa) and ρ_0 the corresponding atmospheric-pressure density.

Many investigators have examined the dependence of the C parameter on temperature. It has generally been found that this parameter is usually either a constant independent of the temperature or a weak function of the temperature. In their work, Dymond and Malhotra [6] showed that for the n-alkanes examined, C could be taken as a constant, equal to 0.2000.

Parameter B definitely varies with temperature, and this has been represented by many investigators by a variety of equations, usually including the critical temperature, T_c, and the critical pressure, P_c. Ginell [8], however, pointed out that B should be equal to $-P_c$ at the critical temperature and showed that this was supported by results for helium. Liquid ammonia densities have been shown also [9] to produce a similar conclusion. Nevertheless, Dymond and Malhotra [6] showed that, for the temperature range up to 0.66 times the critical temperature, a simple quadratic expansion of this parameter as a function of the reduced temperature gave very good results. Dymond and Malhotra [6] further extended their idea by producing a generalized equation for the paremeter B, applied to all n-alkanes up to n-hexadecane except methane and n-pentane (in the latter case no data were available at that time). Their generalized equation was

$$B = 341.539 - 734.292 T_R + 411.189 T_R^2 - (C_n - 6) \tag{2}$$

where T_R is the reduced temperature ($= T/T_c$), and C_n is the actual number of the carbon atoms in the n-alkane molecule.

Since the work of Dymond and Malhotra [6], new experimental data on n-alkane density became available. In particular, new measurements of the density of *n*-pentane and low-temperature measurements of *n*-heptane and *n*-octane enable the reexamination of the equation for the parameter B. We have thus tried to reconsider the case. However, attempts to conform the equation for the B parameter to the Ginell [8] and Kumagai et al. [9] suggestion, that B should be equal to $-P_c$ at the critical temperature, proved unsatisfactory, as this imposed an additional constraint to the generalized form of the equation. We have thus concluded that the quadratic expansion suggested by Dymond and Malhotra [6] is the most suitable form for a simple generalized equation, for temperatures up to 0.7 times the critical temperature.

The liquid density at atmospheric pressure was correlated as [10]

$$\rho_0 = \rho_c \left\{ 1 + \sum_{i=0}^{4} a_i (1 - T_R)^{i/3} \right\} \tag{3}$$

where ρ_c represents the critical density of the liquid. The coefficients a_i and the critical constants are shown in Table I. The coefficients from *n*-pentane to *n*-hexadecane were obtained by Cibulka [10]. In the case of methane to *n*-butane the values were calculated by extrapolating values to atmospheric pressure, simply for consistency in the appearance of the equation.

The final equation obtained for the parameter B is as follows:

$$\text{for } C_2H_6 \text{ to } C_{16}H_{34}, \qquad B = 331.2083 - 713.86 T_R + 401.61 T_R^2 - D \tag{4}$$

Table I. Critical Constants and Coefficients of Eq. (3)

Fluid	ρ_c (kg · m^{-3})	T_c (K)	a_0	a_1	a_2	a_3	a_4
CH_4	162	190.55	−2.892170	19.372430	−25.964817	12.151863	0
C_2H_6	210	305.33	−0.463364	8.930828	−11.154088	5.271987	0
C_3H_8	221	369.85	5.042481	−12.390253	16.563348	−6.601835	0
C_4H_{10}	227	425.25	−0.164000	8.968145	−11.902120	5.914836	0
C_5H_{12}	232	469.80	1.177555	3.891572	−5.508958	3.291806	0
C_6H_{14}	234	507.90	1.597561	1.842657	−1.726311	0.494308	0.646314
C_7H_{16}	236	540.15	1.331593	3.300918	−4.509610	2.765491	0
C_8H_{18}	237	568.95	1.969770	−1.100623	6.364172	−8.693475	4.420047
C_9H_{20}	238	594.90	1.927780	0.930219	−1.334128	1.392823	0
$C_{10}H_{22}$	239	617.65	0.329139	7.364340	−9.985096	5.283608	0
$C_{11}H_{24}$	240	638.85	−0.275532	9.285034	−11.992330	5.969567	0
$C_{12}H_{26}$	240	658.65	−0.030495	8.325350	−10.826840	5.551783	0
$C_{13}H_{28}$	240	676	2.527793	−1.648639	2.100992	0	0
$C_{14}H_{30}$	241	693	3.509916	−4.097681	3.610638	0	0
$C_{15}H_{32}$	241	708	1.088011	1.825236	0	0	0
$C_{16}H_{34}$	241	722	2.613058	−1.999638	2.400114	0	0

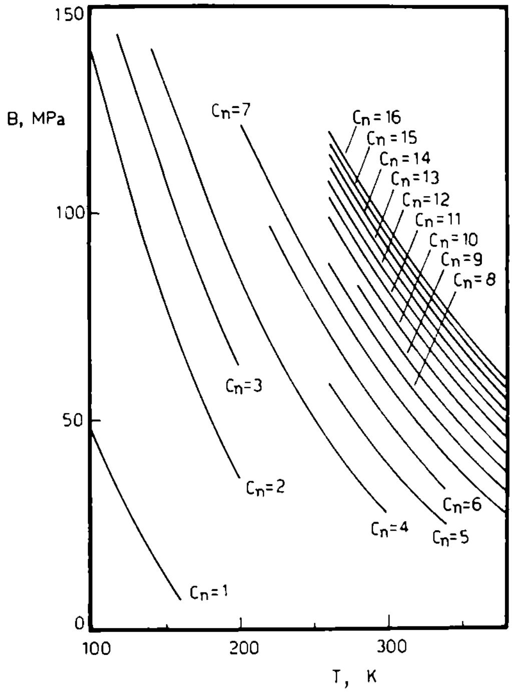

Fig. 1. The dependence of the parameter B upon the absolute temperature, T, and the number of carbon atoms, C_n, in the n-alkane molecule.

where

for C_2H_6 to C_7H_{16}, $D = 0$

for C_8H_{18} to $C_{16}H_{34}$, $D = 0.8\ (C_n - 7)$

and for CH_4,

$$B = 175.8 - 314.57T_R + 134.3T_R^2 \tag{5}$$

The following points ought to be mentioned in relation to the above two equations. From the equation for methane it is apparent that parameter B for methane follows a different dependence in temperature than the rest of the n-alkanes. This is not unusual in the case of the first fluid of an homologous series. In relation to the first equation it is interesting that from ethane to n-heptane, the parameter D is zero. In Fig. 1 the dependence of the parameter B upon the absolute temperature T, is shown for the ranges of experimental measurements.

3. RESULTS

3.1. Pure *n*-Alkanes

In Table II, the experimental measurements [7, 11–28] used to compute the aforementioned equations for the parameter B and the experimental temperature ranges and maximum pressures considered are shown. It should be noted that the maximum pressure shown in the table refers to the point above which deviations started to increase considerably, i.e., the correlation is valid up to the maximum pressure quoted in the table. In most cases this coincides with the maximum experimental pressure. In Table II the average percentage deviation, as well as the maximum percentage deviation for every data set in each *n*-alkane, is also given. The average deviation of all 1939 data points considered is $\pm 0.10\%$, while in only one set of data was a point with a maximum deviation of 0.30% noticed.

The advantages of this new correlation in relation to the very similar one given by Dymond and Malhotra [6] are the following.

(a) Methane is included in the correlation.

(b) New data for the density of *n*-pentane [7] have been included. The Dymond and Malhotra correlation, applied to the new data, produced an average deviation of $\pm 0.35\%$ and a maximum deviation of $\pm 0.75\%$.

(c) New data for the density of *n*-butane [15], *n*-hexane [20], *n*-heptane [21, 24], *n*-octane [20, 26], *n*-dodecane [20], *n*-tetradecane [20], and *n*-hexadecane [23] have been included, in addition to all the data used by Dymond and Malhotra [6].

(d) In most cases the temperature range has been extended to higher values (ethane, propane, butane, *n*-heptane, and *n*-decane). In addition, in some cases low-temperature data available were also included (in *n*-heptane the new data of Muringer et al. [21] allowed the extension of the correlation down to 198 K, while in *n*-octane the new data of Benson and Winnick [26] allowed temperatures down to 258 K to be included).

(e) In most cases the pressure range was extended significantly (propane, *n*-hexane, *n*-octane, *n*-decane, *n*-undecane, *n*-tridecane, and *n*-hexadecane).

For all these reasons, we consider the new correlation presented here to be a good improvement on the work performed by Dymond and Malhotra [6].

Table II. Comparison of Calculated Density Values with Experimental Values for *n*-Alkanes

Fluid	First author	Ref. No.	No. of data points	Temp. range (K)	Pressure max (MPa)	Av. dev. (%)	Max. dev. (%)
CH_4	Diller	11	50	100–140	35	0.06	0.20
	Harris	12	14	110–160	35	0.11	0.20
C_2H_6	Diller	13	61	100–200	35	0.01	0.05
C_3H_8	Diller	14	90	90–200	70	0.11	0.25
C_4H_{10}	Ely	15	73	140–300	35	0.06	0.11
	Diller	16	10	296–298	50	0.06	0.10
C_5H_{12}	Easteal	7	48	278-323	170	0.10	0.22
C_6H_{14}	Dymond	17	10	298-323	300	0.10	0.20
	Kashiwagi	18	76	298-333	115	0.17	0.30
	Mopsik	19	42	233-298	200	0.08	0.17
	Takagi	20	3	298	105	0.07	0.11
C_7H_{16}	Kashiwagi	18	75	298-348	115	0.08	0.23
	Muringer	21	145	198-310	165	0.05	0.22
	Doolittle	22	24	303-373	160	0.06	0.22
	Boelhouwer	23	59	278-393	120	0.10	0.23
	Malhotra	24	86	278-338	205	0.05	0.16
C_8H_{18}	Dymond	25	23	298-348	320	0.08	0.20
	Kashiwagi	18	80	298-348	115	0.07	0.13
	Boelhouwer	23	47	303-393	120	0.08	0.21
	Benson	26	70	258	150	0.10	0.23
	Takagi	20	3	298	105	0.04	0.07
C_9H_{20}	Doolittle	22	24	303-373	160	0.07	0.23
	Boelhouwer	23	48	303-393	120	0.14	0.22
	Grindley	27	78	303–423	125	0.04	0.20
$C_{10}H_{22}$	Dymond	25	11	298-348	350	0.13	0.22
	Kashiwagi	18	79	298-348	115	0.13	0.22
	Snyder	28	75	298-338	500	0.14	0.23
$C_{11}H_{24}$	Doolittle	22	30	303-373	305	0.05	0.20
$C_{12}H_{26}$	Dymond	25	29	298-373	370	0.08	0.21
	Kashiwagi	18	63	298-348	100	0.14	0.26
	Boelhouwer	23	24	303-393	120	0.16	0.29
	Snyder	28	96	298-358	420	0.14	0.26
	Takagi	20	3	298	105	0.05	0.09
$C_{13}H_{28}$	Doolittle	22	30	303-373	305	0.07	0.18
$C_{14}H_{30}$	Snyder	28	117	298-358	370	0.06	0.15
	Takagi	20	2	298	55	0.05	0.07
$C_{16}H_{34}$	Dymond	17	24	298-373	300	0.07	0.15
	Boelhouwer	23	24	303-363	100	0.16	0.27
	Snyder	28	93	298-358	300	0.10	0.28
Total			1939				

3.2. *n*-Alkane Mixtures

The power of the aforementioned Eqs. (1)–(5) can be further demonstrated by considering the density of *n*-alkane mixtures. Dymond and Malhotra [6] used the correlation to predict the pressure dependence of the density of the mixture, knowing the density at atmospheric pressure. To adopt this procedure a mole-fraction average of the factor D and the critical temperature were used [6]. If we adopt the same procedure, then, as expected, we obtain similar results, i.e., a density prediction with an average deviation of ±0.10% and a maximum deviation of ±0.40%.

Since, however, now there are many more density measurements of mixtures of *n*-alkanes, we preferred to examine the prediction of the mixture density from the pure-component density, assuming that no volume change takes place during mixing. The density of the mixtures ρ_{mix}, was therefore calculated from

$$\rho_{\text{mix}} = \frac{\sum_i m_i}{\sum_i V_i} = \left(\sum_i \frac{w_i}{\rho_i}\right)^{-1} \tag{6}$$

where m_i, V_i, and w_i represent the mass, the volume, and the mass fraction of component i.

In Tables III and IV a comparison of measurements of density of binary, ternary, and quaternary mixtures of *n*-alkanes [17, 20, 25, 29–34]

Table III. Comparison of Calculated Density Values with Experimental Values for Binary *n*-Alkane Mixtures

Compounds		First	Ref.	No. of data	Temp. range	Pressure max.	Av. dev.	Max. dev.
1st	2nd	author	No.	points	(K)	(MPa)	(%)	(%)
C_6H_{14}	C_7H_{16}	Chevalier	29	9	298	0.1	0.04	0.05
		Cooper	30	9	293	0.1	0.19	0.25
	C_8H_{18}	Chevalier	29	9	298	0.1	0.06	0.09
		Cooper	30	9	293	0.1	0.21	0.29
	C_9H_{20}	Chevalier	29	9	298	0.1	0.13	0.17
	$C_{10}H_{22}$	Chevalier	29	9	298	0.1	0.17	0.25
		Cooper	30	9	293	0.1	0.28	0.37
		Takagi	20	15	298	105	0.15	0.32
	$C_{12}H_{26}$	Dymond	25	14	298–348	265	0.19	0.35
		Chevalier	29	3	298	0.1	0.14	0.20
	$C_{14}H_{30}$	Chevalier	29	3	298	0.1	0.22	0.30
		Heric	32	10	298	0.1	0.32	0.38
	$C_{16}H_{34}$	Dymond	31	15	283–318	0.1	0.26	0.40
		Dymond	17	52	298–323	300	0.17	0.50
		Chevalier	29	3	298	0.1	0.26	0.35
		Heric	32	20	298	0.1	0.30	0.38

Table III. *(Continued)*

Compounds		First author	Ref. No.	No. of data points	Temp. range (K)	Pressure max. (MPa)	Av. dev. (%)	Max. dev. (%)
1st	2nd							
C_7H_{16}	C_8H_{18}	Chevalier	29	9	298	0.1	0.01	0.02
		Cooper	30	9	293	0.1	0.10	0.12
	C_9H_{20}	Chevalier	29	9	298	0.1	0.04	0.05
	$C_{10}H_{22}$	Chevalier	29	9	298	0.1	0.06	0.08
		Cooper	30	9	293	0.1	0.13	0.16
	$C_{12}H_{26}$	Chevalier	29	3	298	0.1	0.09	0.11
		Cooper	30	9	293	0.1	0.16	0.19
	$C_{14}H_{30}$	Chevalier	29	2	298	0.1	0.13	0.13
		Cooper	30	9	293	0.1	0.20	0.26
	$C_{16}H_{34}$	Chevalier	29	3	298	0.1	0.13	0.18
C_8H_{18}	C_9H_{20}	Chevalier	29	9	298	0.1	0.02	0.06
	$C_{10}H_{22}$	Chevalier	29	9	298	0.1	0.02	0.03
		Cooper	30	9	293	0.1	0.01	0.01
	$C_{12}H_{26}$	Dymond	25	27	298-373	315	0.12	0.40
		Chevalier	29	3	298	0.1	0.04	0.05
		Takagi	20	15	298	105	0.08	0.18
	$C_{14}H_{30}$	Chevalier	29	3	298	0.1	0.04	0.07
		Cooper	30	9	293	0.1	0.10	0.13
		Wakefield	35	10	300-310	0.1	0.06	0.09
	$C_{16}H_{34}$	Chevalier	29	3	298	0.1	0.05	0.08
		Wakefield	33	15	318-338	0.1	0.20	0.30
C_9H_{20}	$C_{10}H_{22}$	Chevalier	29	9	298	0.1	0.03	0.15
	$C_{12}H_{26}$	Chevalier	29	3	298	0.1	0.03	0.05
	$C_{14}H_{30}$	Chevalier	29	3	298	0.1	0.03	0.05
	$C_{16}H_{34}$	Chevalier	29	3	298	0.1	0.04	0.07
$C_{10}H_{22}$	$C_{12}H_{26}$	Chevalier	29	3	298	0.1	0.02	0.03
	$C_{14}H_{30}$	Snyder	34	96	298-358	320	0.19	0.43
		Chevalier	29	3	298	0.1	0.01	0.01
		Takagi	20	15	298	105	0.06	0.20
	$C_{16}H_{34}$	Dymond	25	16	348-373	425	0.11	0.25
		Chevalier	29	3	298	0.1	0.02	0.03
$C_{12}H_{26}$	$C_{14}H_{30}$	Chevalier	29	3	298	0.1	0.01	0.01
	$C_{16}H_{34}$	Snyder	34	84	298-358	330	0.10	0.19
		Chevalier	29	3	298	0.1	0.01	0.01
$C_{14}H_{30}$	$C_{16}H_{34}$	Chevalier	29	3	298	0.1	0.02	0.02
		Cooper	30	9	293	0.1	0.05	0.09
		Heric	32	11	298	0.1	0.09	0.15
Total				648				

Table IV. Comparison of Calculated Density Values with Experimental Values for Ternary and Quarternary *n*-Alkane Mixtures

Mixture	First author	Ref. No.	No. of data points	Temp. range (K)	Pressure Max. (MPa)	Av. dev. (%)	Max. dev. (%)
$C_6H_{14}+C_8H_{18}+C_{16}H_{34}$	Dymond	31	10	288–358	0.1	0.23	0.38
$C_{10}H_{22}+C_{14}H_{30}+C_{16}H_{34}$	Snyder	34	91	298–358	360	0.10	0.20
$C_6H_{14}+C_8H_{18}+C_{12}H_{26}+C_{16}H_{34}$	Dymond	31	5	288–358	0.1	0.25	0.30
Total			106				

with the values produced by this correlation is shown. The average deviation of all the 754 points considered is ±0.13%. As expected, in the extreme case of mixtures of *n*-hexane with *n*-hexadecane, where the volume change is significant, a maximum deviation of ±0.50% is noticed. Considering the fact that in some cases high-pressure measurements were available, the aforementioned equations provide a very good prediction of the density of mixtures of *n*-alkanes.

4. CONCLUSION

A Tait-type equation was used to improve an existing correlation for the density of *n*-alkanes from methane to *n*-hexadecane. The new equation, covering an extended temperature and pressure range, was found able to correlate the density of *n*-alkanes with an average deviation from experimental measurements of ±0.10%.

Assuming no volume change during mixing, the new equation was able to predict the density of a large number of mixtures of *n*-alkanes with an average deviation of about ±0.13%.

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