Prediction of the Density for Natural Gas and Liquefied Natural Gas Mixtures

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Experimental liquid densities and compressibility factors of natural gas and liquefied natural gas mixtures were reproduced using an analytical equation of state, based on the statistical-mechanical perturbation theory of Weeks, Chandler and Andersen. The temperature-dependent parameters of the equation of state were calculated using our previous corresponding-states correlation, based on the normal boiling point parameters. This article shows that the equation of state for multicomponent natural gas and liquefied natural gas mixtures would be predictable with minimal input information, namely the normal boiling temperature and the liquid density at the normal boiling point. The calculated results agreed well with the experiment. From a total of 590 data points for natural gases and 203 data points for liquefied natural gases examined in this work, the average absolute deviations were 0.33% and 2.48%, respectively, and the maximum deviations were 2.63% and 4.61%, respectively.

Introduction

The prediction of the density of natural gas components is an important factor for engineering design, process equipment, material balance equations to simulate petroleum reservoirs, and for performing custody-transfer calculations in the gas industry. Therefore, a study of the p-v-T properties of natural gas is useful both from a practical, and a theoretical, point of view. From a theoretical point of view, having the well-established theoretical tools for predicting the thermophysical properties of fluids is of particular importance, since natural gases are multicomponent mixtures, and developing a theoretical approach for predicting the thermodynamic properties requires, a proper evaluation of the interaction of dissimilar molecules.

At present, perturbation theories offer the most accurate prediction of the equilibrium properties of nonpolar fluids within the framework of statistical thermodynamics. Since the pioneering work of Zwanig (1954), several workers have developed successful theories of a classical equilibrium fluid using perturbation or variational techniques. The perturbation theories consist of Barker and Henderson (1967) and that of Weeks et al. (1971), while the variational methods include the methods by Mansoori and Canfield (1969) and Rasaiah and Stell (1970). In spite of the considerable improvement in these methods, strong theoretical difficulties still remain except for quite simple systems. Most real molecules show anisotropy of shape and permanent multipole moments, thus being more or less outside the scope of these theories.

In recent years, a statistical-mechanical theory has been presented to derive a new analytical equation of state (Song and Mason. 1989, 1990; Ihm et al., 1991). The temperature-dependent parameters of the equation of state can be evaluated by knowing the intermolecular pair potential. The theory has also been developed to mixtures of any number of components (Song, 1990; Ihm and Mason, 1990; Ihm et al., 1992). The pair−potential between unlike molecules plays a central role in the equation of state for mixtures. The main difficulty stems from the fact that such potential energy curves are not accurately known for nearly all systems, except for the noble gases (Boys, 1994). The purpose of this work is to apply the equation of state with less input information than the intermolecular potential energy curve for multicomponent natural gas mixtures. We have shown (Eslami, 2000) that knowing just two more easily measurable parameters is sufficient to predict the equation of state with a good accuracy and simplicity.

Theory

Recent works by Ihm, Song, and Mason on the statistical-mechanical theory of the equation of state for fluids has yielded accurate results for both pure liquids (Song and Mason, 1989, 1990; Ihm et al., 1991) and their mixtures (Song, 1990; Ihm and Mason 1990, Ihm et al., 1992). In the final form, the equation of state for pure substances has the following form

$$\frac{p}{\rho kT} = 1 - \frac{(\alpha - B_2)\rho}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \tag{1}$$

where p is the pressure, ρ is the molar (number) density, B_2 is the second virial coefficient, α is the contribution of the repulsive forces to the second virial coefficient, b is a temperature-dependent parameter analogous to the van der Waals covolume, kT is the thermal energy of one molecule, and λ is an adjustable parameter.

Ihm, Song, and Mason have applied Eq. 1 for single fluids to the mixtures of any number of components (Song, 1990; Ihm and Mason, 1990; Ihm et al., 1992) as

$$\frac{p}{\rho kT} = 1 + \rho \sum_{ij} x_i x_j \left[(B_2)_{ij} - \alpha_{ij} \right] F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \tag{2}$$

with

$$F_{ij} = \frac{1}{1 - \zeta_3} - \left(\frac{d_i d_j}{d_{ij}} \right) \frac{\frac{1}{6}\pi\rho \Sigma_k x_k d_k^2 (4\delta_k + 1)}{(1 - \zeta_3)\left(1 + \frac{2}{3}\pi\rho\Sigma_k x_k d_k^3 \delta_k\right)}, \tag{3}$$

$$G_{ij} = \frac{1}{1 - \zeta_3} + \left(\frac{d_i d_j}{d_{ij}} \right) \frac{\frac{1}{6}\pi\rho \Sigma_k x_k d_k^2 (4\lambda_k - 1)}{(1 - \zeta_3)\left(1 - \frac{2}{3}\pi\rho\Sigma_k x_k d_k^3 \lambda_k\right)}, \tag{4}$$

and

$$\zeta_3 \equiv \frac{1}{6}\pi\rho\Sigma_k x_k d_k^3 \tag{5}$$

where x_i and x_j are mol fractions of components $\delta_k = 0.22\lambda_k$, G_{ij} is the pair distribution function, and summation runs over all components of the mixture. The parameters $(B_2)_{ij}$, α_{ij}, and b_{ij} are all related to the intermolecular potential between ij components, and the parameter d_{ij} is related to b_{ij} via the relation

$$b_{ij} = \frac{2}{3}\pi d_{ij}^3 \tag{6}$$

A knowledge of the intermolecular potential allows the complete specification of the temperature-dependent parameters of the equation of state. Three integrations are needed (Ihm et al. 1992): one to find the second virial coefficient, one to find the scaling factor, and one to find an effective hard-sphere diameter, that is

$$(B_2)_{ij} = 2\pi \int_0^{\infty} \left[1 - \exp\left(-u_{ij}/kT \right) \right] r^2 dr, \tag{7}$$

$$\alpha_{ij} = 2\pi \int_0^{(r_m)_{ij}} \left\{ 1 - \exp\left[(-u_0)_{ij}/kT \right] \right\} r^2 dr, \tag{8}$$

and

$$b_{ij} = 2\pi \int_0^{(r_m)_{ij}} \left\{ 1 - \left[1 + (u_0)_{ij}/kT \right] \exp\left[(-u_0)_{ij}/kT \right] \right\} r^2 dr \tag{9}$$

where $(u_0)_{ij}$ is the repulsive branch of u_{ij} defined as (Weeks et al., 1971)

$$(u_0)_{ij}(r) = \begin{cases} u_{ij}(r) + \epsilon_{ij}, & r \le (r_m)_{ij}, \\ 0, & r > (r_m)_{ij}, \end{cases} \tag{10}$$

and ϵ_{ij} and $(r_m)_{ij}$ are the potential well-depth and the position of minimum in u_{ij}, respectively. We predict the equation of state for multicomponent natural gases with less input information than the full intermolecular potentials.

Determination of Parameters with Minimum Information

Although the knowledge of intermolecular pair potential between interacting molecules is an important factor in determining the equation of state, it is shown (Tao and Mason 1992, Boushehri and Mason 1993, Ghatee and Boushehri

Table 1 Composition of Natural Gases

	Mixture Number								
Components	1	2	3	4	5	6	7	8	9
Hydrogen							0.00010	0.00010	0.00009
Helium							0.00137	0.00133	0.00126
Oxygen							0.00010	0.00010	0.00009
Nitrogen	0.1209		0.02693	0.0004	0.00038	0.00036	0.01639	0.01586	0.01503
Methane	0.6265	0.80078	0.88269	0.8926	0.84351	0.80334	0.88639	0.85794	0.81279
Ethane	0.2526	0.11641	0.06115	0.02260	0.02136	0.02034	0.02935	0.02841	0.02691
Propane		0.06530	0.00998	0.0106	0.01002	0.00954	0.01963	0.01900	0.01900
Butane		0.01750	0.00989				0.00952	0.00922	0.00873
Isobutane				0.0001	0.00010	0.00009	0.00952	0.00922	0.00873
Pentane							0.00314	0.00304	0.00288
Isopentane							0.00304	0.00295	0.00279
Carbon dioxide			0.00936	0.0429	0.04054	0.03861	0.00294	0.00285	0.00270
Propylene				0.0001	0.00010	0.00009	0.00010	0.0001	0.00009
Hydrogen sulfide				0.0305	0.02882	0.02745			
Carbonyl sulfide				0.0001	0.00010	0.00009			
Water				0.0001	0.05510	0.10009	0.01850	0.05000	0.10000

1996, Eslami 2000) that the equation is usable with much less input than the full intermolecular forces, since the scaling factor α and the effective diameter b are universal functions of temperature when expressed in suitable reduced units (Ihm et al., 1991).

The experimental second virial coefficient data can be used to calculate the Boyle temperature and the Boyle volume. Song and Mason (1989, 1992) have shown that the Boyle volume can be used as a source of scaling constant for reducing α and b, and the Boyle temperature can be used as a scaling constant for reducing temperature. When reduced in this manner, the dimensionless plots of α/v_B and b/v_B vs. T/T_B are universal functions and empirical formulas (Song and Mason 1992), and numerical tables (Ihm et al., 1991) for these parameters are available.

In addition to knowing the experimental values of the second virial coefficients, there are several correlation schemes based on the law of corresponding states, by which the second virial coefficients can be predicted with reasonable accuracy. One of the best correlations, developed by Pitzer and Curl (1957) for nonpolar fluids and later extended to mixtures of low polarity by Schreiber and Pitzer (1990), requires the critical constants plus the Pitzer acentric factor. In this correlation it is shown that plots of the dimensionless second virial coefficient, $B_2 p_c/RT_c$ vs. the dimensionless temperature T/T_C, form a universal family of curves, which can be

Table 2. Calculated Densities of Natural Gases vs. Experimental Data[*]

Mixture	T (K)	Δp (bar)	$\Delta \rho$ (mol$\cdot$L^{-1})	NP[*]	AAD (%)[*]	MD (%)[*]
1[†]	275.00	1 000-603.328	0.04388-18.8307	45	0.822	2.634
	310.00	1.000-588.209	0.03888-17.1041	52	0.479	1.721
	345.00	1.000-604.997	0.03491-15.6028	46	0.215	1.475
2[‡]	298.15	1.3472-160.801	0.05456-9.5978	18	0.549	2.548
	323.15	1.363-135.5652	0.05087-6.6052	17	0.335	1.530
3[‡]	298.15	1.2083-123.7313	0.04886-6.3408	17	0.046	0.116
	323.15	1.8604-150.0941	0.06946-6.653	16	0.078	0.158
4[§]	323.15	1.5552-99.5024	0.0579-4.2579	12	0.198	0.525
	348.15	1.6752-110.9384	0.0384-4.2533	12	0.201	0.532
	373.15	1.7933-122.2265	0.05785-4.2486	12	0.207	0.538
	398.15	1.9126-133.4307	0.05779-4.24397	12	0.212	0.542
	423.15	2.0299-144.5443	0.05772-4.2320	12	0.210	0.583
	448.15	2.1478-155.5621	0.05766-4.2341	12	0.211	0.611
	473.15	2.2652-166.5025	0.057600-4.22964	12	0.212	0.644
5[§]	348.15	1.1629-3.7110	0.040186-0.12875	4	0.098	0.128
	373.15	1.2452-12.6462	0.04014-0.41219	7	0.121	0.218
	398.15	1.3278-29.0750	0.04010-0.89490	9	0.168	0.421
	423.15	1.4100-66.4849	0.04006-1.94286	11	0.292	0.879
	448.15	1.4918-153.4545	0.04001-4.21641	13	0.391	1.010
	473.15	1.5731-164.348	0.039970-4.21162	13	0.456	1.675
6[§]	348.15	0.96190-3.1139	0.033400-0.10804	4	0.139	0.359
	373.15	1.0330-7.2691	0.03336-0.23605	6	0.161	0.423
	398.15	1.1028-16.8576	0.03332-0.51570	8	0.197	0.499
	423.15	1.1703-38.8284	0.033293-1.12662	10	0.243	0.682
	448.15	1.2383-8.91913	0.03325-2.46061	12	0.471	1.421
	473.15	1.3032-140.3491	0.033220-3.63405	13	0.576	2.148
7[§]	348.15	1.1152-11.5006	0.03857-0.4029	7	0.087	0.148
	373.15	1.1944-26.6471	0.03853-0.8797	9	0.116	0.283
	398.15	1.2732-61.3119	0.03849-1.92032	11	0.211	0.407
	423.15	1.3520-142.4265	0.03845-4.1909	13	0.337	1.249
	448.15	1.4300-153.4466	0.03841-4.1863	13	0.312	1.195
	483.15	1.5404-168.7308	0.03835-4.1795	13	0.315	1.189
8[§]	348.15	0.6521-2.1086	0.02261-0.04944	4	0.201	0.275
	373.15	0.6978-7.2835	0.02259-0.23632	7	0.218	0.321
	398.15	0.7432-24.8556	0.02256-0.76346	10	0.243	0.501
	423.15	0.7879-57.2282	0.02254-1.6677	12	0.269	0.621
	448.15	0.8337-132.6185	0.0251-3.6419	14	0.384	1.216
	483.15	0.8970-145.5059	0.2248-3.6361	14	0.515	1.659
9[§]	373.15	0.3618-3.7468	0.0116-0.1213	7	0.399	0.825
	398.15	0.3864-8.7077	0.01158-0.26491	9	0.412	0.931
	423.15	0.4103-29.5949	0.01157-0.8556	12	0.437	1.020
	448.15	0.4334-68.0910	0.01156-1.86851	14	0.610	1.827
	483.15	0.4678-161.9173	0.1154-4.0775	16	0.831	2.487
Overall				590	0.334	2.634

[*] The last three columns represent the number of points, average absolute deviation, and maximum deviation, respectively.
[†] Experimental data from Staby et al. (1991).
[‡] Experimental data from Biswas et al. (1990).
[§] Experimental data from Eubank et al. (1987).

indexed by the acentric factor for different substances. However, the critical constants for most systems are not known accurately.

Several other correlation schemes are proposed for the calculation of the second virial coefficient of nonpolar fluids (Boushehri and Mason, 1993; Ghatee and Boushehri, 1996; Eslami, 2000). Utilizing these correlations, it is shown (Boushehri and Mason, 1993; Ghatee and Boushehri, 1996; Eslami, 2000) that the equation of state of nonpolar fluids can be predicted by knowing two scaling constants, one to make a dimensionless second virial coefficient, and one to make a dimensionless temperature.

Recently, a corresponding-states correlation for the second virial coefficient of nonpolar fluids was developed by Eslami (2000), with even less input information and normal boiling point constants than the others (Pitzer et al., 1957, Schreiber and Pitzer, 1990, Boushehri and Mason, 1993; Ghatee and Boushehri 1996). The correlation has been employed (Eslami, 2000) to predict the equation of state of a large number of nonpolar fluids including noble gases, diatomic molecules, saturated hydrocarbons, and a number of aliphatic, aromatic, and cyclic hydrocarbons over a wide range of temperatures and pressures within an accuracy of a few percent. Determination of the temperature-dependent parameters of the equation of state by this procedure also self-adjusts the parameter λ to 0.495 (Eslami, 2000). While the present method uses less input information than the others and is easier to apply, it is shown that it has nearly the same predictive power as the previous methods (Tao and Mason, 1992, Boushehri and Mason, 1993, Ghatee and Boushehri, 1996). Our proposed correlation reads as

$$B_2\,\rho_{bp} = 1.033 - 3.0069\left(\frac{T_{bp}}{T}\right) - 10.588\left(\frac{T_{bp}}{T}\right)^2 + 13.096\left(\frac{T_{bp}}{T}\right)^3 - 9.8968\left(\frac{T_{bp}}{T}\right)^4 \tag{11}$$

where ρ_{bp} is the liquid density at the normal boiling temperature T_{bp}. Knowing the second virial coefficient from Eq. 11, the parameters α and b can be calculated by rescaling the empirical formulas by Song and Mason (1992) in terms of normal boiling point constants. The results are shown to be of the form (Eslami 2000)

$$\alpha\rho_{bp} = a_1\left\{\exp\left[-c_1\left(\frac{T}{T_{bp}}\right)\right]\right\} + a_2\left\{1-\exp\left[-c_2\left(\frac{T_{bp}}{T}\right)^{1/4}\right]\right\}. \tag{12}$$

and

$$b\rho_{bp} = a_1\left[1-c_1\left(\frac{T}{T_{bp}}\right)\right]\exp\left[-c_1\left(\frac{T}{T_{bp}}\right)\right] + a_2\left\{1-\left[1+0.25c_2\left(\frac{T_{bp}}{T}\right)^{1/4}\right]\exp\left[-c_2\left(\frac{T_{bp}}{T}\right)^{1/4}\right]\right\}. \tag{13}$$

where

$$a_1 = -0.0860, \qquad c_1 = 0.5624$$

$$a_2 = 2.3988, \qquad c_2 = 1.4267.$$

Specifying the temperature-dependent parameters in this manner, we have shown (Eslami, 2000) that the equation of state for single substances is put to the much simpler form

$$\frac{p}{\rho kT} = 1 - \frac{(\alpha - B_2)\rho}{1+0.11b\rho} + \frac{\alpha\rho}{1-0.495b\rho} \tag{14}$$

Table 3. Calculated vs. Experimental (Staby and Mollerup, 1991) Data of Compressibility Factor for Mixture No. 1 at 275 K and 345 K

$T = 275.00$ K				$T = 345.00$ K			
p (bar)	Z_{cal}	Z_{expt}.	D (%)	p (bar)	$Z_{\text{cal.}}$	$Z_{\text{expt.}}$	D (%)
1.000	0.99677	0.99662	0.015	1.000	0.99854	0.99855	−0.001
6.168	0.97963	0.97907	0.057	5.048	0.99241	0.99271	−0.029
12.304	0.95892	0.95893	−0.001	12.527	0.98118	0.98204	−0.086
24.967	0.91487	0.91380	0.117	17.559	0.97371	0.97496	−0.128
31.454	0.89071	0.89084	−0.015	27.354	0.95937	0.96145	−0.215
42.448	0.85123	0.85160	−0.040	38.023	0.94417	0.94722	−0.321
60.498	0.78290	0.78753	−0.587	52.601	0.92430	0.92879	−0.483
78.798	0.71482	0.72676	−1.643	84.256	0.89958	0.90621	−0.731
95.520	0.68001	0.68092	−0.133	99.484	0.87161	0.88123	−1.091
102.027	0.64934	0.66691	−2.634	137.111	0.84832	0.86103	−1.475
125.994	0.62911	0.63667	−1.187	172.088	0.84538	0.85764	−1.429
136.758	0.62381	0.63289	−1.433	193.984	0.85206	0.86322	−1.292
187.941	0.68273	0.67281	1.475	256.100	0.89677	0.90442	−0.845
218.519	0.73365	0.71643	2.403	302.968	0.94589	0.95534	−0.989
443.317	1.14619	1.12433	1.945	457.907	1.14166	1.1459	−0.369
603.328	1.43241	1.40133	2.218	604.997	1.33909	1.35183	−0.942

The present method for calculating the second virial coefficient and the other two temperature-dependent parameters can be extended to mixtures by using a simple geometric mean for the boiling point temperature and an arithmetic mean for the liquid density at the boiling point, that is

$$(T_{bp})_{ij} = \left[(T_{bp})_i (T_{bp})_j\right]^{1/2} \qquad (15)$$

and

$$(\rho_{bp})_{ij} = \frac{1}{2}\left[(\rho_{bp})_i^{-1/3} + (\rho_{bp})_j^{-1/3}\right]^{1/3} \qquad (16)$$

Evaluating the temperature-dependent parameters of the equation of state using Eqs. 11−13, 15, and 16, one can put the equation of state for mixtures in the operative mode.

Results and Discussion

We have used a large body of experimental data in order to check the ability of the present equation of state for predicting the density of natural gas and liquefied natural gas mixtures. The compositions of studied natural gas mixtures are listed in Table 1. The calculated density for a ternary natural gas mixture of nitrogen-methane-ethane (mixture No. 1) at 275 K, 310 K, and 345 K, and pressures up to 600 bar, are compared with the experimental data of Staby and

Table 4. Composition of Liquefied Natural Gases

No.	Nitrogen	Methane	Ethane	Propane	Butane	$i-$Butane	Pentane	i-Pentane
1	0.04752	0.95248						
2	0.30349	0.69651						
3	0.49242	0.50758						
4	0.05933		0.94067					
5	0.02014			0.97986				
6	0.03794			0.96206				
7	0.06740			0.93260				
8		0.35457	0.64543					
9		0.49325	0.50675					
10		0.68006	0.31994					
11		0.29538		0.70462				
12		0.49637		0.50363				
13		0.74920		0.25080				
14		0.85796		0.14204				
15		0.48687				0.51313		
16		0.58828			0.41172			
17		0.91674			0.08326			
18			0.50105	0.49895				
19			0.67287	0.32713				
20			0.68939			0.31061		
21			0.72436			0.27564		
22			0.65343		0.34657			
23			0.67117		0.32883			
24				0.49030		0.50970		
25				0.50326		0.49674		
26				0.58692	0.41308			
27				0.60650	0.39350			
28				0.60949	0.39051			
29					0.52961	0.47039		
30	0.05931	0.89071			0.04998			
31		0.86040	0.04600	0.04790		0.04570		
32		0.85378	0.05178	0.04703		0.04741		
33		0.085133	0.05759	0.04808	0.04300			
34		0.84566	0.07924	0.05060	0.02450			
35	0.04801	0.80940	0.04542	0.05050		0.04667		
36	0.02628	0.81249	0.08484	0.04931	0.02708			
37		0.85892	0.11532	0.01341	0.00705	0.00530		
38		0.84558	0.08153	0.04778	0.01252	0.01259		
39	0.00601	0.90613	0.06026	0.02154	0.00306	0.00300		
40	0.00973	0.88225	0.07259	0.02561	0.00492	0.00490		
41	0.01383	0.85934	0.08477	0.02980	0.00707	0.00519		
42		0.85341	0.07898	0.04729	0.00992	0.00854	0.00089	0.00097
43		0.75442	0.15401	0.06950	0.01057	0.00978	0.00083	0.00089
44	0.00859	0.75713	0.13585	0.06742	0.01326	0.01336	0.00216	0.00223
45	0.00801	0.74275	0.16505	0.06547	0.00893	0.00843	0.00067	0.00069
46	0.00599	0.90068	0.06537	0.02200	0.022284	0.00291	0.00011	0.00010

Experimental data for mixtures No. 1-29, and No. 30-46 are taken from Hiza et al. (1977) and Haynes (1982), respectively.

Mollerup (1991). Also, the data for two samples of simulated natural gases (Nos. 2,3) at 298.15 K and 323.15 K, and pressures of up to 160 bar, have been calculated and compared with the experimental data of Biswas et al. (1990). The experimental data on the densities of two natural gases, one sweet and one sour, with varying amount of water up to 10% (No. 4–9) by Eubank et al. (1987) are also well reproduced by the present equation of state. The results for all mixtures are tabulated in Table 2. For carbon dioxide, which has not a normal boiling point, the triple point temperature and the liquid density at the triple point are used for the calculation of the temperature-dependent parameters from Eqs. 11–13. Although Table 2 itself represents the degree of consistency of our calculations with experiment, the results for Mixture No.1, as a typical example, at two isotherms are shown in Table 3, in which any pattern of deviation is more obvious.

Analysis of our predicted results in Tables 2 and 3 shows that the present equation of state is capable of accurately predicting the density of multicomponent natural gas mixtures at any temperature and pressure. For example, the wet natural gas mixture with 10% water, No. 9, is a fourteen-component mixture with 10% of a polar substance. The

Table 5. Calculated Molar Density of Liquefied Natural Gases in (Table 4) vs. Experimental Data (Hiza et al. 1977, Haynes 1982)

No.	ΔT (K)	Δp (bar)	$\Delta \rho$ (mol·L^{-1})	NP	AAD (%)	MD(%)
1	105.00–140.00	1.38–9.20	23.2809–26.8476	8	1.69	2.73
2	100.00–120.00	3.45–10.11	24.5737–26.8735	5	1.51	2.42
3	95.00–130.00	3.30–21.10	22.1005–27.081	8	1.48	2.82
4	105.00–120.00	3.85–6.38	20.8998–21.4718	4	0.55	1.02
5	110.00–115.00	3.57–4.71	16.0931–16.2131	2	1.21	1.42
6	105.00–110.00	4.95–6.71	16.3410–16.4638	2	1.43	1.54
7	100.00–105.00	6.31–8.80	16.7084–16.8055	2	1.62	1.87
8	105.00–130.00	0.256–1.55	21.9441–23.1032	6	1.56	1.98
9	105.00–140.00	0.325–3.55	22.0765–23.9619	8	2.21	2.49
10	105.00–130.00	0.416–2.62	23.5007–25.1027	6	2.65	2.80
11	105.00–110.00	0.27–0.409	18.3624–18.5132	2	3.57	3.99
12	105.00–130.00	0.384–2.32	19.5546–20.4909	6	0.89	1.44
13	105.00–130.00	0.478–3.03	22.1019–23.4768	6	2.76	3.54
14	105.00–130.00	0.516–3.30	23.2461–24.9622	6	3.64	3.79
15	110.00–125.00	0.629–1.852	16.9156–17.3575	4	2.27	3.48
16	120.00–130.00	1.636–3.183	18.3058–18.6495	4	0.50	0.77
17	105.00–140.00	0.513–5.844	22.6391–25.1536	8	3.01	3.31
18	105.00–140.00	4.38×10^{-4}–0.019	17.3526–18.3618	8	2.31	3.71
19	125.00–140.00	6.72×10^{-3}–0.026	18.1509–18.6192	4	0.51	1.08
20	115.00–120.00	1.17×10^{-3}–2.41×10^{-3}	17.2344–17.3716	2	3.17	3.53
21	105.00-130.00	5.33×10^{-4}–9.40×10^{-3}	17.2825–17.9779	4	3.21	3.59
22	115.00–120.00	1.11×10^{-3}–2.28×10^{-3}	17.0824–17.2184	2	3.87	4.05
23	110.00–140.00	5.17×10^{-3}–0.030	16.6947–17.5047	6	2.64	3.86
24	105.00–130.00	3.21×10^{-5}–3.98×10^{-4}	13.8342–14.3080	6	2.83	3.34
25	125.00–130.00	2.18×10^{-4}–4.01×10^{-4}	13.8737–13.9718	2	3.31	3.40
26	110.00–140.00	1.17×10^{-4}–4.91×10^{-4}	14.0786–14.6839	3	4.00	4.61
27	140.00–150.00	4.99×10^{-4}–6.21×10^{-4}	13.9346–14.1343	3	3.12	3.67
28	115.00–120.00	1.66×10^{-4}–1.99×10^{4}	14.5521–14.6487	2	4.35	4.59
29	125.00–140.00	4.50×10^{-6}–8.10×10^{-5}	12.4447–12.6943	4	3.19	3.40
30	110.00–125.00	2.400–5.196	24.1141–25.3450	4	2.89	3.26
31	115.00–135.00	1.186–4.320	22.8637–24.2654	4	3.27	3.27
32	115.00–130.00	1.191–3.238	23.1834–24.2100	4	3.26	3.40
33	115.00–135.00	1.180–4.301	22.9634–24.3243	5	3.31	3.52
34	115.00–130.00	1.167–3.201	23.5204–24.5569	4	3.49	3.63
35	115.00–130.00	3.005–6.125	23.0893–24.1487	4	3.28	3.31
36	115.00–130.00	2.214–4.793	23.3954–24.4562	4	3.26	3.42
37	115.00–130.00	1.185–3.225	23.9490–25.0957	4	2.59	2.91
38	115.00–130.00	1.166–3.188	23.5154–24.5586	4	3.18	3.23
39	115.00–130.00	1.478–3.722	24.1578–25.3834	4	1.97	2.49
40	115.00–125.00	1.639–3.022	24.4022–25.2023	3	2.62	2.83
41	115.00–130.00	1.812–4.222	23.8981–25.0384	4	2.73	2.90
42	110.00–130.00	0.787–3.210	23.5883–25.0063	5	3.36	3.51
43	115.00–125.00	0.723–2.153	23.3351–24.2529	4	3.12	3.25
44	115.00–130.00	1.155–3.744	22.9514–24.1809	5	3.28	3.39
45	115.00–125.00	1.158–2.853	23.3804–24.3141	4	3.17	3.29
46	115.00–130.00	1.456–3.698	24.1289–25.3600	4	2.05	2.53
Overall				203	2.48	4.61

The last three columns represent the number of data points, average absolute deviation, and the maximum deviation, respectively.

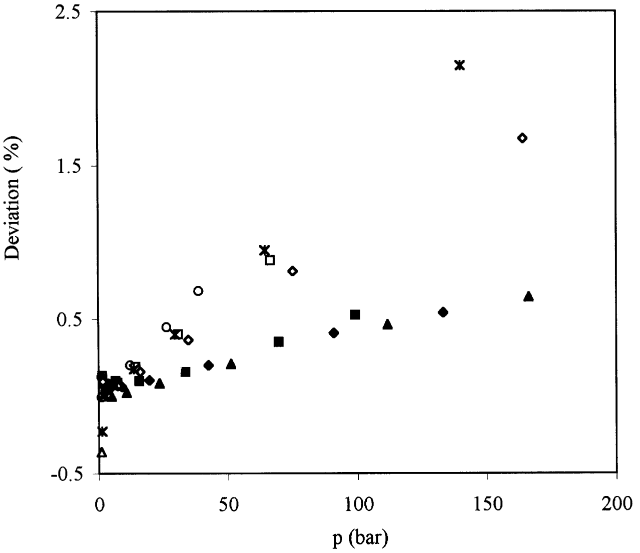

Figure 1. Deviation percent, $(\rho_{Cal.}-\rho_{Expt.})\times 100/\rho_{Expt}$ for the density of natural gas mixtures.

No. 4 at 323.15 K (■), 423.15 K (♦), and 473.15 K (▲); No. 5 at 348.15 K (●), 423.15 K (□), and 473.15 K (◇); and No. 6 at 348.15 K (△), 423.15 K (○), and 473.15 K (∗) compared with the experimental data.

equation of state can still predict the density of this mixture in the temperature range of 373.15 K to 583.15 K and pressures up to 160 bar, within a few percent. The overall average absolute deviation and the maximum deviation for 590 data points listed in Table 2 are 0.334% and 2.634%, respectively. It is worth noting that as the mol fraction of water increases, the results tend to be less accurate. This stems from the fact that the present correlation for the second virial coefficient, and, hence, the other two temperature-dependent parameters, α and b, are given for nonpolar fluids.

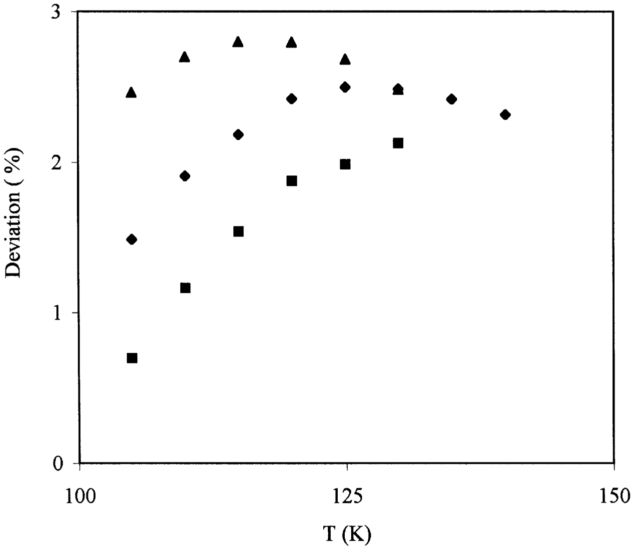

Figure 2. Deviation plot for the orthobaric liquid density of liquefied natural gas mixtures.

No. 8 (■), No. 9 (♦), and No. 10 (▲).

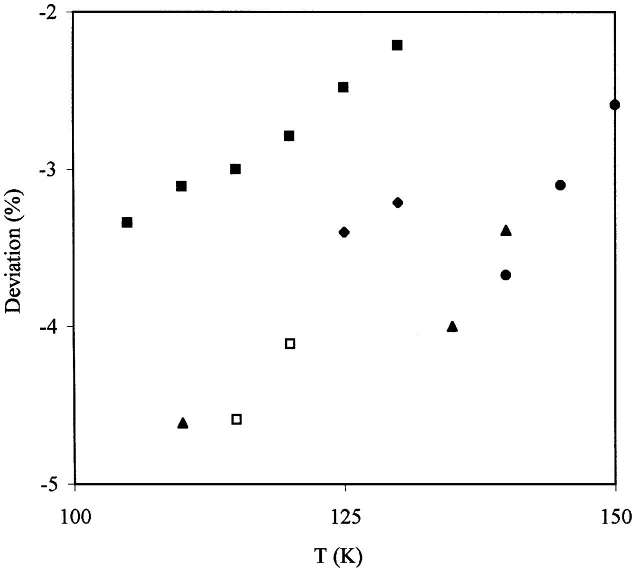

Figure 3. The same as Figure 2 for mixtures.

No. 24 (■), No. 25 (♦), No. 26 (▲), No. 27 (●), and No. 28 (□).

The equation of state is also employed to predict the liquid density of a large number of liquefied natural gases listed in Table 4. The experimental data for orthobaric liquid densities given by Hiza et al. (1977) and Haynes (1982) for multicomponent liquefied natural gas mixtures in the temperature range of 105–140 K has been calculated and the results are summarized in Table 5. For mixtures No., 17–29, for which the experimental vapor pressures data are not available, the simple Raoult's law is applied to calculate the vapor pressure. As is clear from the results in Table 5, the agreement with experimental data (Hiza et al. 1977; Haynes, 1982) is good. The average absolute deviation and the maximum deviation for 203 data points tabulated in Table 4 are 2.48% and 4.61%, respectively.

In addition to the summarized results in Tables 2, 3, and 5, which elucidate the predictive power of the present equation for the prediction of the density of natural gas and liquefied natural gas mixtures, the deviation plots for some systems may help one to find out how the equation passes through phase space. We have selected three systems consisting of mixtures No. 4–6, No. 8–10, and No. 24–28, for which the present equation of state works very well, works average, and works less well, respectively. The results for the aforementioned mixtures are plotted in Figures 1–3, respectively.

Although the compounds studied in this work have a variety of complexities, and, hence, different intermolecular forces, Eqs. 3 and 4 for α and b, respectively, which have been obtained (Eslami, 2000) using the results of a simple Lennard–Jones potential, can still reproduce the experimental data well. The reason is that the parameters α and b depend only on the repulsive branch of the potential energy function and are insensitive to the details of the intermolecular forces (Ihm et al., 1991). Thus, statistical-mechanical perturbation theory can be applied to determine the equation of state of real fluids if the intermolecular forces are known. However, for real fluids the equation of state can be used with much less input information than the full potential, because the temperature-dependent parameters of the equation of state that depend only on the repulsion α and b, are insensitive to the detailed shape of the potential, and can be scaled with two fixed constants T_B and υ_B, or in our procedure by T_{bp} and ρ_{bp}.

Finally, the present method does not need the critical parameters, which are scarce for many substances and are subject to higher experimental uncertainties than those of the normal boiling point parameters. Also, it does not need such properties as the heat of vaporization (Boushehri and Mason, 1993) or surface tension (Ghatee and Boushehri, 1996). Furthermore, the present equation of state is simpler than the others (Tao and Mason 1992, Boushehri and Mason 1993, Ghatee and Boushehri 1996) in that the parameters λ_i are all equal and self-adjusted to 0.495.

Notation

a_1, a_2, c_1, c_2 = constants in Eqs. 12 and 13
b = analogous to the van der Waals covolume, m^3
B_2 = second virial coefficient, m^3
d = an effective hard-sphere diameter, m
F = a dimensionless parameter defined by Eq. 3
G = a dimensionless parameter defined by Eq. 4
K = Boltzmann's constant, $J \cdot K^{-1}$
p = pressure, bar
r = interparticle distance, m
T = temperature, K
u = intermolecular potential, J
u_0 = the repulsive branch of u defined by Eq. 10, J
x = mol fraction
Z = compressibility factor

Greek symbols

α = a scaling factor defined by Eq. 8
δ = 0.22 λ
ζ_3 = a dimensionless parameter defined by Eq. 5
λ = an adjustable parameter
ρ = molar density, $dm^3 \cdot mol^{-1}$

Subscripts

bp = boiling point
i = substance i
j = substance j
ij = pairwise ij
m = minimum

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Manuscript received Jan. 23, 2001, and revision received May 7, 2001.