International Journal of Thermophysics, Vol. 20, No. 6, 1999

Application of New, Modified BWR Equations of State to the Corresponding-States Prediction of Natural Gas Properties[1]

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The accurate description of mixtures includes both single-phase (bulk) properties and the location of phase equilibrium boundaries, e.g., properties that depend upon partial molar properties. In order to estimate these properties, many variants of corresponding-states theory have been developed, especially for nonpolar mixtures such as those found in natural gas systems. In this work we have developed two new, modified BWR equations of state for two natural gas components (*n*-pentane and *n*-heptane) and used these equations in a reformulated (Teja-like) Lee–Kesler model. The reformulated model has been tested on bulk-phase properties of hydrocarbon systems, in both the pure and the mixed states. Results have been obtained using the original Lee–Kesler model, the extended corresponding-states theory, and the multifluid corresponding-states principle using several combinations of reference fluids chosen from this and previous equation of state studies. Details of the new equations of state and theoretical comparisons are reported.

KEY WORDS: corresponding states; density; equation of state; Lee–Kesler; natural gas mixtures; *n*-heptane; *n*-pentane.

1. INTRODUCTION

Accurate methods for calculating thermodynamic and volumetric properties of pure substances and their mixtures are essential in natural gas engineering. If available, experimental data could (and should) be used in

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Coloarado, U.S.A.

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0195-928X/99/1100-1721$16.00/0

these applications. Unfortunately, in many cases, the necessary data are either nonexistent or scarce and one must generate design data by the use of suitable correlations or theories or both.

Thermodynamic correlations can be classified into two broad categories: fluid specific correlations and generalized correlations. In their most general form, fluid specific correlations are equations of state developed from wide-range experimental data for a given compound. They can provide excellent representations of thermodynamic behavior in the range of the experimental database but extrapolation outside the experimental data range must be done with care since these equations have little or no theoretical basis. Many mathematical equation of state (EOS) formulations have been proposed, with one of the more popular forms being the 32-term, modified Benedict–Webb–Rubin (MBWR32) equation of state. In this work, new MBWR32 equations of state were generated to represent the thermodynamic behavior of *n*-pentane and *n*-heptane. We note that the same functional form has been used to represent the thermodynamic surfaces of many fluids, including a series of light hydrocarbons by Younglove and Ely [1] and in our previous extended corresponding states study [2].

Of the many generalized correlation approaches that have been proposed, the three-parameter corresponding-states principle (CSP) has proved to be the most powerful method for predicting properties of fluids and mixtures. Generally, this principle takes one of two forms: a one-fluid (single reference fluid) version, which may incorporate extensions with shape factors, or a multifluid version, which usually incorporates two nonspherical reference fluids. In this report we have chosen to investigate the multifluid CSP (MFCSP) using our newly developed MBWR32 equations of state. The MFCSP was originally proposed by Pitzer et al. [3–5]. It was modified by Lee and Kesler [6] explicitly to include a heavy reference fluid and more recently by Teja et al. [7, 8] to eliminate the need for a simple fluid as one of the references. We have performed calculations using three pairs of reference fluids: methane and propane, methane and pentane, and propane and pentane. In addition, we present brief comparisons with the single reference fluid extended corresponding-states theory (ECST). All of the models are used to predict the properties of *n*-heptane and other hydrocarbon systems.

2. EQUATION-OF-STATE DETERMINATION

The parameters for the MBWR32 equations of state were determined using multiproperty regression analysis to fit various types of experimental data simultaneously. Data types used in the fitting process were single-phase ($P\rho T$) data, isobaric heat capacity, isochoric heat capacity, saturation heat capacity, sound velocity, and vapor pressures and orthobaric densities. Ancillary equations were generated for the latter three quantities so that they could be used in the fitting process at uniform temperatures. In addition, the ideal gas heat capacity was correlated with an approximate statistical mechanical formula. The functional forms of the ancillary and ideal gas functions are as follows.

Vapor pressure:

$$\ln \frac{p_s}{p_c} = \frac{a_1 \tau + a_2 \tau^{3/2} + a_3 \tau^{5/2} + a_4 \tau^5}{T_r} \tag{1}$$

Liquid density:

$$\frac{\rho_l}{\rho_c} = 1 + \frac{b_1 \tau^{\beta} + b_2 \tau^2 + b_3 \tau^3}{1 + b_4 \tau^{1-\beta}} \tag{2}$$

Vapor density:

$$Z_v - 1 = \frac{(Z_c - 1)\ p_r}{T_r^4} (1 + c_1 \tau^{\beta} + c_2 \tau + c_3 \tau^2 + c_4 \tau^3) \tag{3}$$

Heat capacity:

$$\frac{C_p^0(T)}{R} = 4 + \sum_{j=1}^{3} d_j e^{\Theta_j/T} \left(\frac{\Theta_j/T}{e^{\Theta_j/T} - 1} \right)^2 \tag{4}$$

In these equations the subscript "r" denotes a quantity divided by the corresponding critical property, $\tau = (1 - T_r)$, and Z denotes the compressibility factor, pV/RT. Table I lists the critical properties and values of the coefficients for Eqs. (1)–(4) for both n-pentane and n-heptane. The functional form of the MBWR32 equation is given as a polynomial,

$$p = \rho RT + \sum_{i=1}^{32} a_i \rho^{r_i} T^{s_i} e^{-\gamma_i (\rho/\rho_c)^2} \tag{5}$$

and Table II gives the values of the exponents appearing in Eq. (5) and the parameter values (a_i) for the two pure fluids studied in this work.

2.1. n-Pentane

In this work we have improved our previous wide-range representation of n-pentane [2] by considering an expanded range of data in the

Table I. Critical Properties and Ancillary Equation Parameters for *n*-Pentane and *n*-Heptane

Parameter	*n*-Pentane	*n*-Heptane
Critical point:		
T_c (K)	469.650	540.150
P_c (MPa)	3.36456	2.7388
ρ_c ($\mathrm{mol \cdot L^{-1}}$)	3.2155	2.341
Vapor pressure, Eq. (1)		
a_1	−7.25890225563	−7.86757094657
a_2	1.63588194193	2.09162387105
a_3	−2.03861805642	−3.06685283337
a_4	−3.02657377877	−3.41366147194
Liquid density, Eq. (2)		
b_1	2.076773601640	2.152711448500
b_2	−0.412306577146	−0.332345782803
b_3	0.372318994620	0.372321985297
b_4	−0.292630247698	−0.270526655801
β	0.35	0.35
Vapor density, Eq. (3)		
c_1	−0.978921999326	−0.786494824876
c_2	0.288054758485	−1.165549769620
c_3	−0.827003918743	4.064706491380
c_4	1.168124931620	−2.957543499080
β	0.35	0.35
Ideal gas C_p^0, Eq. (4)		
d_1	9.751560716	15.29994054
d_2	22.71445741	31.86604737
d_3	11.65392685	14.10640675
Θ_1	404.8796661	401.5547607
Θ_2	1785.491483	1813.365387
Θ_3	4504.430788	5041.869289

equation-of-state development. Some of the other more recent equations of state for *n*-pentane include those of Starling [9], Das et al. [10], Teja and Singh [11], Gehrig and Lentz [12], Kratzke et al. [13], and Grigor'ev et al. [14, 15]. With the exception of Ref. 14, all of these previous equations have focused on a subset of the *PVT* surface, for example, the critical region or a region of the *PVT* surface that was studied experimentally by the authors. Thus, most of the previous equations are not directly comparable to the one developed in this study.

Table II. MBWR-32 Parameters for *n*-Pentane and *n*-Heptane [Eq. (5)][a]

i	r_i	s_i	γ_i	a_i, Pentane	a_i, Heptane
1	2	1	0	$-7.41533782499 \times 10^{-3}$	$-9.53769631187 \times 10^{-3}$
2	2	$\frac{1}{2}$	0	$7.54044021950 \times 10^{-1}$	$9.72551866385 \times 10^{-1}$
3	2	0	0	$-1.93328401588 \times 10^{+1}$	$-2.60081304889 \times 10^{+1}$
4	2	-1	0	$3.39428034054 \times 10^{+3}$	$5.20865382062 \times 10^{+3}$
5	2	-2	0	$-5.12571561595 \times 10^{+5}$	$-1.07729056282 \times 10^{+6}$
6	3	1	0	$1.51195406963 \times 10^{-4}$	$-6.20474297014 \times 10^{-4}$
7	3	0	0	$-7.12225059892 \times 10^{-1}$	2.08733258744
8	3	-1	0	$4.12664185793 \times 10^{+2}$	$-1.37572781583 \times 10^{+3}$
9	3	-2	0	$8.40258305443 \times 10^{+4}$	$6.95627225584 \times 10^{+4}$
10	4	1	0	$-4.68416651753 \times 10^{-5}$	$1.90615930406 \times 10^{-4}$
11	4	0	0	$3.03565637672 \times 10^{-1}$	$-5.61551412281 \times 10^{-1}$
12	4	-1	0	$-1.42146321204 \times 10^{+2}$	$2.73983005070 \times 10^{+2}$
13	5	0	0	$-1.10170659283 \times 10^{-2}$	$6.28902715950 \times 10^{-2}$
14	6	-1	0	$-9.80664356304 \times 10^{-1}$	$-1.11012478028 \times 10^{+1}$
15	6	-2	0	$1.10979804446 \times 10^{+2}$	$6.22600247144 \times 10^{+2}$
16	7	-1	0	$2.98029604130 \times 10^{-1}$	1.57273923084
17	8	-1	0	$-1.41484307201 \times 10^{-2}$	$-6.63204129629 \times 10^{-2}$
18	8	-2	0	-3.39208006239	$-1.79732347053 \times 10^{+1}$
19	9	-2	0	$2.08782048763 \times 10^{-1}$	1.24881866033
20	3	-2	1	$5.38055429992 \times 10^{+4}$	$3.81777590060 \times 10^{+5}$
21	3	-3	1	$-6.40401885304 \times 10^{+7}$	$-3.56280298214 \times 10^{+7}$
22	5	-2	1	$-1.19676622034 \times 10^{+4}$	$1.75658356410 \times 10^{+4}$
23	5	-4	1	$1.71973349582 \times 10^{+9}$	$4.54695406896 \times 10^{+9}$
24	7	-2	1	$-3.06383363882 \times 10^{+2}$	$2.05985406654 \times 10^{+3}$
25	7	-3	1	$1.43168348944 \times 10^{+5}$	$8.72406003683 \times 10^{+5}$
26	9	-2	1	1.41452433419	$5.62265877351 \times 10^{+1}$
27	9	-4	1	$-2.52955687564 \times 10^{+6}$	$-3.20150071052 \times 10^{+7}$
28	11	-2	1	$-3.85316416299 \times 10^{-1}$	3.57524917645
29	11	-3	1	$2.65416349789 \times 10^{+2}$	$3.27649699126 \times 10^{+3}$
30	13	-2	1	$4.76643876980 \times 10^{-4}$	$-1.15729200586 \times 10^{-1}$
31	13	-3	1	$-8.37595968663 \times 10^{-1}$	$3.93007045330 \times 10^{+1}$
32	13	-4	1	$-1.35160880503 \times 10^{+2}$	$3.88225605345 \times 10^{+3}$

[a] Units of the equations of state are MPa, liter, mol, and K. The universal gas constant was set as $R = 0.00831451\ \mathrm{MPa \cdot L \cdot mol^{-1} \cdot K^{-1}}$.

Table III presents statistical comparisons of Eqs. (1)–(3) with selected data for the *n*-pentane saturation boundary. Generally, the vapor pressures and liquid densities are represented to ±0.05% and saturated vapor densities to within ±0.3%. The new MBWR32 equation of state for *n*-pentane is based on data covering the temperature range of 173 to 573 K with pressures to 284 MPa. The critical temperature and density calculated from the equation of state agree with those values given in Table I but the

Table III. Comparison of Primary n-Pentane Saturation Data with Ancillary Equations

Source	No. of points used/total	Temperature range (K)	AAD (%)	BIAS (%)	RMS (%)
Vapor pressure, Eq. (1)	78/83	142–469	0.039	0.002	0.056
Beattie et al. [21]	5/5	373–448	0.061	−0.061	0.021
Li and Canjar [22]	2/2	423–448	0.060	−0.060	0.043
Sage et al. [23]	3/4	344–444	0.026	−0.022	0.016
Sage and Lacey [24]	3/5	311–444	0.050	−0.048	0.060
Willingham et al. [25]	9/9	286–310	0.009	−0.008	0.006
Hossenlopp and Scott [26]	9/9	259–331	0.014	0.014	0.008
Osborn and Douslin [27]	15	269–341	0.015	0.015	0.009
Hill [28]	17/19	393–469	0.071	−0.053	0.108
Kratzke et al. [13]	14/14	350–460	0.067	0.063	0.038
Calc. from C_{sat}	1/1	142	0.006	−0.006	–
Liquid density, Eq. (2)	78/82	149–469	0.036	0.003	0.047
Orrit and Laupretre [29]	21/21	149–249	0.025	0.021	0.026
Legatski [30]	5/6	224–255	0.050	0.032	0.082
Kratzke et al. [13]	12/12	237–440	0.047	0.037	0.039
Mel'nikov et al. [31]	10/10	153–433	0.035	−0.035	0.070
Holcomb et al. [32]	28/28	241–409	0.033	−0.018	0.038
Grigor'ev et al. [15]	2/5	449–469	0.018	0.036	0.018
Vapor density, Eq. (3)	46/48	200–460	0.122	−0.010	0.231
Sage et al. [23]	3/5	310–444	0.107	−0.082	0.065
Sage and Lacey [24]	4/4	327–378	0.077	−0.006	0.103
Virial intersection[a]	16/16	200–350	0.017	−0.017	0.011
Rectilinear diameter[b]	23/23	350–460	0.206	0.003	0.323

[a] Calculated by intersection of the virial surface with the vapor pressure equation.

[b] Calculated by construction of a rectilinear diameter estimate with the liquid density equation.

calculated critical pressure is slightly lower, 3.357 MPa. Comparisons with data not used in the fit indicate that the equation should be reliable to temperatures of 900 K. Table IV summarizes the *PVT*, specific heat, and sound speed data for the primary n-pentane data sets and presents a summary of the deviations of these data from the MBWR32 EOS. The experimental data for n-pentane are plentiful but exhibit large systematic differences in regions of overlap. Our equation was "anchored" to the saturation boundary and the data reported by Kratzke et al. [13] The low-temperature single-phase density data of Vasil'ev [16] were extrapolated to the vapor pressure curve and the resulting saturated liquid densities were found to differ systematically from Eq. (2) by 0.2%. Thus, all of Vasil'ev's data were

Table IV. Comparison of Primary Single-Phase *PVT*, Specific Heat, and Sound Speed Data for *n*-Pentane

Date type and source	No. of points	Data ranges			Deviation (%)		
		T (K)	P (MPa)	ρ (mol · L $^{-1}$)	AAD	BIAS	RMS
PVT[a]							
Grigor'ev et al. [15]	118	453–523	3–14.4	1.37–5.54	1.093	−0.378	1.711
					0.225	0.074	0.305
Kumurov et al. [33]	128	373–648	0.19–12	0.06–3.65	0.409	0.003	0.575
					0.323	0.002	0.452
Kratzke, et al. [13]	119	238–574	0.75–60.6	5.84–9.41	0.122	−0.046	0.497
					2.995	1.1811	0.08
Scaife and Lyons [34]	121	248–373	7.4–284	8.27–10.3	0.108	0.060	0.126
					1.457	−0.192	1.788
Vasil'ev [16]	142	173–448	0.62–149	5.68–10.7	0.152	0.008	0.182
					12.22	0.889	29.81
C_{sat}							
Messerly et al. [35]	25	148–303			0.997	0.930	1.026
C_p							
Hossenlop and Scott [26]	40	298–525	0.05–0.20		0.183	0.047	0.231
Peng and Stiel [36]	170	333–422	2.76–20.7		1.138	0.037	1.332
Sound speed							
Belinskii and Ikramov [37]	39	293–313	0.10–637		0.389	−0.157	0.485
Laniez et al. [38]	220	263–433	0.60–213		0.386	−0.371	0.310
Otpushchennikov et al. [39]	109	303–393	0.10–203		0.413	0.369	0.255
2nd virial coefficient[b]							
Beattie et al. [40]	6	473–573			3.049	2.047	3.999
McGlashan and Potter [41]	6	358–414			8.147	−6.198	8.901
Hajjar et al. [42]	10	323–473			6.188	2.168	8.901
Kurumov et al. [33]	12	373–648			3.870	0.479	4.619
Xueqin et al. [43]	6	308–348					

[a] *PVT* deviations are given as two lines. The top line gives density deviations, while the bottom line gives pressure deviations.

[b] Second virial coefficent deviations are given as $dm^3 \cdot mol^{-1}$.

shifted by this amount to make them consistent with the saturation boundary. The extensive data reported by Gehrig and Lentz [12] were not used in developing the equation of state due to inconsistencies of up to 1.7% with other data.

Overall, the equation represents the single-phase density to within 0.5% except near the critical point where the density uncertainties increase to 2%. The pressure is represented to within ±4% except in the low-temperature liquid region. Heat capacities are reproduced to within 1.5% and the sound velocity is represented to within 0.4%.

2.2. *n*-Heptane

Relatively few equation of state studies have been reported for *n*-heptane. Other than our preliminary MBWR32 equation [2] we have found only the BWRS equation reported by Starling [9] and the critical region equation of Kurumov [17], neither of which is directly comparable to the MBWR32 reported here. As in the case of *n*-pentane, the difference between our new MBWR32 equation and our previous version is that a wider range and more accurate thermodynamic data have been included in the fitting process.

Table V. Comparison of Primary *n*-Heptane Saturation Data with Ancillary Equations

Source	No. of points used/total	Temperature range (K)	AAD (%)	BIAS (%)	RMS (%)
Vapor pressure, Eq. (1)	147/154	299–540	0.048	0.003	0.058
McMicking and Kay [44]	13/19	372–540	0.053	0.016	0.064
Willingham et al. [25]	39/40	299–372	0.044	0.030	0.037
Forziati et al. [45]	20/20	299–372	0.039	0.024	0.038
Weber [46]	61/61	335–503	0.042	−0.002	0.054
Wisniewska et al. [47]	14/14	400–471	0.090	−0.090	0.031
C_{sat} [48]	14/14	185–300	1.347	−0.161	1.561
Liquid density, Eq. (2)	86/91	183–533	0.040	0.000	0.048
Doolittle [49]	4/5	303–473	0.039	−0.020	0.037
Christopher et al. [50]	12/12	298–353	0.044	0.006	0.048
Scaife and Lyons [34]	9/9	248–373	0.040	0.006	0.048
Mel'nikov et al. [31]	10/11	193–523	0.035	0.008	0.042
Kuss and Taslimi [51]	4/4	298–353	0.038	0.038	0.010
Young [52]	24/27	273–533	0.027	−0.003	0.033
Dornte and Smyth [53]	10/10	183–363	0.070	−0.011	0.075
Mirskaya and Kamilov [54]	13/13	373–503	0.044	−0.007	0.051
Vapor density, Eq. (3)	38/40	200–533	1.065	0.117	1.892
Barile and Thodos [55]	11/11	351–526	0.679	0.522	0.793
McMicking and Kay [44]	5/7	473–533	3.024	−1.100	3.470
Virial intersection[a]	10/10	200–380	0.036	−0.017	0.067
Kay [56]	7/7	420–532	0.898	−0.010	1.302
Zawisza and Vejrosta [57]	5/5	423–523	2.246	0.888	2.982

[a] Calculated by intersection of the virial surface with the vapor pressure equation.

Table VI. Comparison of Primary Single-Phase *PVT*, Specific Heat, and Sound Speed Data for *n*-Heptane

		Data ranges			Deviation (%)		
Date type and source	No. of points	T (K)	P (MPa)	ρ (mol · L^{-1})	AAD	BIAS	RMS
PVT[a]							
Smith et al. [58]	81	303–623	0.72–35.6	1–7.01	0.363	−0.080	0.657
					7.645	6.854	15.44
Grigor'ev et al. [59]	108	423–623	0.17–5.47	0.05–2.36	0.404	−0.008	0.482
					0.288	0.063	0.324
Eduljee et al. [60]	40	273–333	50.7–508	6.93–8.61	0.101	−0.048	0.108
					1.234	0.623	1.331
Scaife and Lyons [34]	129	248–373	7.0–100	6.20–7.67	0.113	0.112	0.078
					5.453	−5.418	6.361
Kuss and Taslimi [51]	20	298–353	39.2–196	6.72–7.77	0.068	0.062	0.046
					1.211	−1.146	1.064
Kuss [61]	60	298–353	9.8–196	6.41–7.85	0.129	0.109	0.138
					2.940	−2.686	3.550
Ozawa et al. [62]	42	298–348	9.9–196	6.47–7.72	0.095	−0.047	0.105
					2.085	0.199	3.135
Doolittle [49]	46	303–573	5–200	4.80–7.77	0.219	−0.197	0.226
					2.948	2.481	2.556
Vasil'ev [63]	222	188–523	0.55–147	3.96–7.93	0.110	−0.069	0.122
					6.812	3.616	13.29
Muringer et al. [64]	206	198–311	10.1–263	6.77–8.31	0.020	−0.005	0.024
					0.508	−0.059	0.864
Nichols et al. [65]	87	278–511	0.91–69.1	4.40–7.41	0.151	−1.131	0.135
					2.640	1.728	2.791
C_v							
Sun et al. [66]	105	205–310		7.43–8.11	1.694	1.694	0.625
C_{sat}							
Douglas et al. [48]	35	185–510			0.574	0.278	0.655
Amirkhanov et al. [67]	36	373–535			0.570	0.281	0.653
C_p							
Grigor'ev et al. [59]	9	303–462	0.10–1.00		0.638	−0.163	0.638
Sun et al. [66]	105	205–310	0.10–260		1.617	1.617	0.717
Sound speed							
Muringer et al. [64]	113	185–310	0.1–263		0.110	0.081	0.121

[a] *PVT* deviations are given as two lines. The top line gives density deviations, while the bottom line gives pressure deviations.

Table V presents statistical comparisons of Eqs. (1)–(3) with selected data for the *n*-heptane saturation boundary. Generally, the vapor pressures are represented to within ±0.05%, liquid densities to within ±0.06%, and saturated vapor densities to within ±2%. As one would expect, there is a great deal of uncertainty in the saturated vapor densities, especially at the higher temperatures. The new MBWR32 equation of state for *n*-heptane is based on data in the temperature range of 188 to 673 K with pressures to 507 MPa. Preliminary indications are that it can be safely applied to temperatures as high as 1000 K, although data at the higher temperatures are somewhat unreliable. The critical point parameters calculated from the equation of state coincide with the values given in Table I. Table VI summarizes the *PVT*, specific heat, and sound speed data for the primary *n*-heptane data sets and presents a summary of the deviations of these data from the MBWR32 EOS. Generally the equation of state represents the density to within ±0.2% and pressure to within ±4%, although the pressure deviations can be large in the low-temperature, high-density region. Heat capacities are typically represented to within ±1.5% and the liquid sound velocity data are represented to within ±0.12%.

3. MULTIFLUID CORRESPONDING STATES

As mentioned in the Introduction, the multifluid corresponding-states model was originally proposed by Pitzer et al. [3–5] in a tabular correlation and was extended in an analytical form by Lee and Kesler [6]. Teja et al. [7, 8] proposed a version of the theory that does not require the use of a simple fluid as one of the reference fluids. In particular, the compressibility factor of the target fluid is given by

$$Z(T_r, P_r) = Z^{(1)}(T_r, P_r) + \frac{\omega - \omega^{(1)}}{\omega^{(2)} - \omega^{(1)}} [Z^{(2)}(T_r, P_r) - Z^{(1)}(T_r, P_r)] \qquad (6)$$

where ω is Pitzer's acentric factor and T_r and P_r are the reduced temperature and pressure of the target fluid. This equation may be considered to be a Taylor series expansion of the compressibility factor in terms of the acentric factor. In applying this model, the two reference fluids [denoted by superscripts 1 and 2] are evaluated at different reduced volumes but the same reduced temperature and pressure as the target fluid. The model may be extended to mixtures by using the van der Waals one-fluid mixing rules to calculate the critical properties of the target fluid:

$$T_{c_m} V_{c_m} = \sum_i \sum_j x_i x_j T_{c_{ij}} V_{c_{ij}} \tag{7}$$

$$V_{c_m} = \sum_i \sum_j x_i x_j V_{c_{ij}} \tag{8}$$

$$Z_{c_m} = \sum_i x_i Z_{c_i} \tag{9}$$

$$\omega_m = \sum_i x_i \omega_i \tag{10}$$

In Eqs. (7)–(10) the subscript m denotes a mixture value and the ij terms are calculated using Lorentz–Berthelot mixing rules with binary interaction parameters ξ_{ij} and η_{ij}, *viz.*, $T_{c_{ij}} V_{c_{ij}} = \xi_{ij} (T_{c_i} V_{c_i} T_{c_j} V_{c_j})^{1/2}$ and $V_{c_{ij}} = \eta_{ij} (V_{c_i}^{1/3} + V_{c_j}^{1/3})^3/8$.

3.1. Results for Hydrocarbon Densities

To test the usefulness of our new MBWR32 equations we have performed a series of density comparisons for four pure hydrocarbons (C_2, nC_6, nC_7, and nC_{10}) and five methane-containing binary mixtures ($C_1 + C_2$, $C_1 + C_3$, $C_1 + nC_4$, $C_1 + nC_7$, $C_1 + nC_{10}$). In the case of the mixtures, the binary interaction parameters were set equal to unity. The comparisons were performed for the original Lee–Kesler model and for the Teja model with several combinations of MBWR32 reference fluids: methane/propane, methane/pentane, and propane/pentane. The methane and propane MBWR32 equations were reported previously by Younglove and Ely [1].

The results of the comparisons are summarized in Table VII. We have also included in this table results obtained from the extended corresponding-states theory (ECST) using a propane reference and generalized shape factors [18]. We see that for the pure fluids investigated, $C_3 + nC_5$ MBWR32 implementation gives improved results compared to the original Lee–Kesler (LK) model. An exception (as one might expect) is that the $C_1 + C_3$ reference pair gives substantially better results for predicting the density of pure ethane. For light mixtures where the size ratios are low, the $C_1 + C_3$ reference pair gives improved results compared to the original LK model. However, as the size ratio increases in the mixture, original LK model performs substantially better than the models based on the MBWR32 equations. This is especially true for the $C_1 + nC_{10}$ system, where the original LK model gives results that are of the order of 1 % more accurate. It is difficult to draw any conclusions from the comparison of the ECST results with those from the MFCSP approach. Table VII does show, however, that there always seems to be a pair of MFCSP reference fluids

Table VII. Corresponding-States Predictions for Hydrocarbon Systems[a]

System	N	MLK reference fluid				ECST
		LK	$C_1 + C_3$	$C_1 + C_5$	$C_3 + C_5$	C_3
C_2	1386	1.034	0.344	0.470	0.525	0.317
		−0.236	−0.064	0.065	−0.181	−0.112
		2.175	1.374	2.138	0.728	0.063
nC_6	1808	1.264	1.192	0.736	0.708	0.801
		−0.504	−0.37	0.241	0.255	−0.436
		3.134	2.778	2.923	2.066	1.146
nC_7	1151	1.044	1.707	0.783	0.546	1.196
		−0.879	−1.243	−0.427	−0.066	−1.108
		1.635	1.933	1.029	0.921	1.127
nC_{10}	1196	1.361	3.327	1.835	1.326	1.891
		−0.559	−1.171	−0.12	0.701	−1.859
		1.931	4.339	2.468	1.837	1.378
$C_1 + C_2$	1717	1.293	0.954	0.978	0.988	1.070
		−1.143	−0.807	−0.801	−0.645	−1.041
		1.619	1.622	1.666	2.028	1.233
$C_1 + C_3$	922	1.181	1.158	1.234	1.444	1.450
		−0.098	0.374	0.401	0.435	−0.937
		2.168	2.213	2.234	2.361	1.641
$C_1 + nC_4$	1683	1.71	1.360	1.408	1.272	1.495
		−1.481	−0.951	−0.747	−0.759	−1.283
		1.86	1.926	2.089	1.988	1.357
$C_1 + nC_7$	382	1.121	1.420	1.691	1.455	1.995
		0.23	0.938	1.666	1.423	−1.940
		3.614	3.629	3.549	3.385	1.103
$C_1 + nC_{10}$	502	0.884	1.567	1.98	1.916	0.808
		0.317	1.151	1.965	1.91	0.925
		1.056	1.431	1.128	1.106	2.019

[a] The first row for each system shows average absolute percentage deviations, the second shows average percentage deviations, and the third gives the root-mean-square percentage deviations about the mean.

which yield slightly better results than the single reference fluid ECST approach.

These results suggest ways in which the MFCSP might be improved. The first is that the pure fluid results might be improved by including a second order term in the Taylor series expansion, Eq. (6). This should allow for a better simultaneous representation of both the light and heavy hydrocarbons. We are currently exploring this possibility using the base of MBWR32 equations that we have developed.

The second area for improvement has to do with the interaction between the mixing rules and functional form of the equation of state. In particular, the results observed for the more asymmetric mixtures must reflect the interaction between the mixing rules and the functional forms of the equations of state. The MBWR32 equation has temperature dependence up to T^{-5}, while the LK equation has only T^{-3}. The hard-sphere expansion theory [19] suggests that van der Waals mixing rules are accurate only to order T^{-1}. Thus, the simpler the temperature dependence of the equation of state, the greater the accuracy of Eqs. (7) and (8). Given this conclusion, it seems that the theory would benefit from reference fluid equations that retain the accuracy of the MBWR32 equation but have a simpler temperature dependence. We are also investigating this possibility of using our equation-of-state optimization selection algorithm methodology [20].

Finally, it would be interesting to explore the introduction of shape factors into the MFCSP approach. This would provide a "custom" reference fluid for each system that could then be fine-tuned with component shape factors.

4. SUMMARY AND CONCLUSIONS

In this work we have developed new high-accuracy, wide-range equations of state for *n*-heptane and *n*-pentane. In addition to their usefulness as stand-alone equations, we have also explored their use as reference fluids in the MFCSP. The latter study led us to the conclusion that the MFCSP approach should be extended by including a second-order term, and efforts should be undertaken to develop high accuracy equations of state which have a relatively simple temperature dependence. In addition, the approach might be improved for mixtures by introducing component shape factors into the MFCSP mixing rules. Work is under way to achieve all of these goals.

ACKNOWLEDGMENTS

J.R. thanks the Royal Thai government for financial support of this work through a fellowship. J.F.E. acknowledges support of the U.S. Department of Energy, Office of Basic Energy Sciences, Grant DE-FG03-95ER41568.

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