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Corresponding-States Modeling of the Speed of Sound of Long-Chain Hydrocarbons[1]

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Models based on the corresponding-states principle have been extensively used for several equilibrium and transport properties of different pure and mixed fluids. Some limitations, however, have been encountered with regard to its application to long chain or polar molecules. Following previous studies, where it was shown that the corresponding-states principle could be used to predict thermophysical properties such as vapor–liquid interfacial tension, vapor pressure, liquid density, viscosity, and thermal conductivity of long-chain alkanes, the application of the corresponding-states principle to the estimation of speeds of sound, with a special emphasis on the less studied heavier *n*-alkane members, is presented. Results are compared with more than four thousand experimental data points as a function of temperature and pressure for *n*-alkanes ranging from ethane up to *n*-hexatriacontane. Average deviations are less than 2%, demonstrating the reliability of the proposed model for the estimation of speeds of sound.

KEY WORDS: corresponding-states; high pressure; model; *n*-alkanes; paraffinic wax; speed of sound.

1. INTRODUCTION

Due to the continuous oil depletion and its increasing cost, heavier oil fractions not previously extracted due to technical and economical reasons, are now receiving increasing interest [1, 2]. For the correct design of

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the extraction and processing of these heavier oils, several thermophysical properties such as density, viscosity, vapor pressure, thermal conductivity, and interfacial tension are required. While some measurements have been performed, models are still necessary in order to cover all the required thermodynamic conditions.

The speed of sound is a thermophysical property that can accurately be determined in broad ranges of temperature and pressure, and that can be related with other thermodynamic quantities such as density, heat capacity, and isentropic and isothermal compressibilities:

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

$$\kappa_T = \kappa_S + \frac{T\alpha_p^2}{\rho C_P} \tag{2}$$

$$\rho(T, p) = \rho(p_{\mathrm{atm}}, T) + \int_{p_{\mathrm{atm}}}^{p} \frac{1}{u^2}\, dp + T \int_{p_{\mathrm{atm}}}^{p} \frac{\alpha_p^2}{C_p}\, dp \tag{3}$$

where κ_S and κ_T are, respectively, the isentropic and isothermal compressibilities, ρ is the density, α_P is the cubic expansion coefficient, u is the speed of sound, T is the temperature, C_P is the isobaric heat capacity, and subscript atm stands for atmospheric conditions.

Due to its high measuring accuracy, the speed of sound is an excellent source of data for some derived properties in broad temperature and pressure ranges that otherwise would be very difficult to measure. For these reasons, speed-of-sound data have also been selected by several authors to fit equation-of-state parameters [3–5].

Among the different models for the estimation of speeds of sound, the corresponding-states theory, namely the Lee–Kesler approach [6] has proved to be one of the most accurate models [7–9], although some large deviations have been recently found for the heavier *n*-alkanes [9].

Recently, a new corresponding-states model has been successfully proposed for several equilibrium (vapor pressure, liquid density, liquid–vapor interfacial tension) and transport properties (thermal conductivity, viscosity) of both pure *n*-alkanes and their asymmetric mixtures [10–16], and some petroleum fractions used as raw material for the production of diesels [17]. In this work, the same framework is proposed for the estimation of the available *n*-alkane speed-of-sound data in the reduced-temperature $0.3 \le T_{\mathrm{r}} = \frac{T}{T_{\mathrm{c}}} \le 1.0$ and reduced-pressure $0.0 \le p_{\mathrm{r}} = \frac{p}{p_{\mathrm{c}}} \le 305.6$ ranges, where subscript c denotes critical property. As will be shown, the corresponding-states principle is an adequate tool for the accurate estimation of speeds of sound.

2. CORRESPONDING-STATES PRINCIPLE

Following its initial empirical formulation by van der Waals, the corresponding-states principle has evolved in order to deal with several non-spherical and polar molecules. Its success is grounded on the accuracy obtained in broad temperature and pressure conditions and its strong theoretical basis [18–23], while mathematically simple and using a minimum amount of experimental information. One of its advantages is that the same formalism can be used for different properties, whereas the only changes are the definition of the reduced property, the equations used for the reference systems, and the reference system itself. Since these models do not use any experimental data for the estimated property of the target fluid, they are also predictive. The only experimental information required for the target fluid includes the critical properties and the Pitzer acentric factor.

The application of corresponding-states models extends from equilibrium properties such as vapor pressure [24–28], liquid density [11, 26, 28–30], or surface tension [12, 13, 15, 16, 26, 31, 32] to transport properties such as viscosity [11, 26, 33–36] and thermal conductivity [14, 26, 37–39].

In its original form, the reduced compressibility factor (Z_{r}) was expressed in terms of a universal function of two parameters, the dimensionless temperature (T_{r}) and molar volume (V_{r}) (or pressure, p_{r}):

$$Z_{\mathrm{r}_j}(T_{\mathrm{r}}, V_{\mathrm{r}}) = Z_{\mathrm{r}_0}(T_{\mathrm{r}}, V_{\mathrm{r}}) \tag{4}$$

$$T_{\mathrm{r}} = \frac{T}{T_{\mathrm{c}}}, \quad V_{\mathrm{r}} = \frac{V}{V_{\mathrm{c}}}, \quad p_{\mathrm{r}} = \frac{p}{p_{\mathrm{c}}} \tag{5}$$

where Z is the compressibility factor, pV/RT, and the subscripts j and 0 stand for target and spherical reference fluid, respectively.

Experimental evidence has, however, shown that this two-parameter corresponding-states approach was limited to the noble gases and nearly spherical molecules such as nitrogen, oxygen, and methane. To extend this theory to a broader range of fluids, additional characterization parameters have been introduced to account for the non-conformalities. One of the approaches performs a multi-parameter Taylor's series expansion of the property of interest about the new parameters. An additional third parameter, the Pitzer acentric factor, ω, was initially introduced [25] to generalize the scope of the corresponding-states principle including fluids whose force fields slightly depart from those of the original spherical symmetry. Reduced pressure was used instead of reduced volume due to the uncertainty usually ascribed to the measurement of critical volumes. A Taylor series expansion of the property of interest is performed about this third parameter, with the series being usually truncated beyond the first derivative:

$$Z_{r_j}\,(T_r, p_r, \omega) = Z_{r_0}\,(T_r, p_r) + \omega Z_{rr}\,(T_r, p_r) \tag{6}$$

where Z_{r_0} has the same meaning as in Eq. (4) and Z_{rr} is a function that represents the departure from the spherical symmetry, the derivative $^{\partial Z}/_{\partial\omega}$. In spite of the analytical formalism of Eq. (6), values for the functions Z_{r_0} and Z_r were only presented in tabular form by Pitzer and co-workers.

With the advent of cheaper and faster computers, Lee et al. [6] suggested replacing the derivative in the Taylor series with its finite difference:

$$Z_{r_j}\,(T_r, p_r, \omega) = Z_{r_0}\,(T_r, p_r) + \frac{\omega_j}{\omega_1}\left[Z_{r_1}\,(T_r, p_r) - Z_{r_0}\,(T_r, p_r)\right] \tag{7}$$

with subscript 1 representing a non-spherical reference fluid ($\omega > 0$).

Although this new formalism contained a correction for the departure from the spherical symmetry, some problems arose in the description of polar or asymmetric systems. Since Eq. (7) still contains a spherical reference fluid, ($\omega = 0$), large interpolations/extrapolations were frequent in the description of real fluids. Another problem was related with the widespread use of methane as the spherical reference fluid. Since methane has a triple point relatively high compared with the majority of the hydrocarbons, some low temperature calculations would result in the extrapolation of the methane equation of state introducing considerable errors in the predicted data.

Following Teja and coworkers [28, 30–32, 36, 39–41], the spherical reference fluid in Eq. (7) was abandoned. Therefore, two reference fluids could be similar to the evaluating fluid, reducing the errors due to large interpolations/extrapolations. Several thermophysical properties were estimated according to this new framework with very good predictive results;

$$X_{r_j} = X_{r_1} + \frac{\omega_j - \omega_1}{\omega_2 - \omega_1}(X_{r_2} - X_{r_1}) \tag{8}$$

where X_{r_j} stands for the reduced property to be evaluated and subscripts 1 and 2 for the two reference fluid properties at the same reduced conditions as those of the target fluid. In all cases, good agreement with experimental data was obtained in the range of fluids covered by the two references. However, considerable deviations can be found if the reference fluids are far apart in the series from the target fluid, either interpolating or extrapolating [10, 11, 13, 14]. In an attempt to correct for these deviations, and based on the dependence of the desired properties with ω (or chain length), the Taylor series expansion of the reduced property was carried out to the second-order term:

$$X_{r_j} = X_{r_1} + D_1(\omega - \omega_1) + D_2(\omega - \omega_1)(\omega - \omega_2)$$

$$D_1 = \frac{X_{r_2} - X_{r_1}}{\omega_2 - \omega_1}, \qquad D_2 = \frac{\frac{X_{r_3} - X_{r_1}}{\omega_3 - \omega_1} - \frac{X_{r_2} - X_{r_1}}{\omega_2 - \omega_1}}{\omega_3 - \omega_1} \tag{9}$$

A third reference fluid is introduced with the advantage that no change in the reference system has to be done while studying a large range of fluids or an asymmetric mixture. If instead, the Teja approach (Eq. (8)) is adopted for asymmetric mixtures with a single reference system, considerable deviations resulting from large interpolations/extrapolations may be found as was already shown for vapor–liquid interfacial tension, liquid density, viscosity and thermal conductivity [10, 11, 13, 14].

The extension of the model for mixtures is straightforward using the one-fluid concept through the following mixing and combining rules:

$$\omega_{\mathrm{cm}} = \sum_i x_i \omega_i \tag{10}$$

$$V_{\mathrm{cm}} = \sum_i \sum_j x_i x_j V_{\mathrm{c}ij} \tag{11}$$

$$T_{\mathrm{cm}} V_{\mathrm{cm}} = \sum_i \sum_j x_i x_j T_{\mathrm{c}ij} V_{\mathrm{c}ij} \tag{12}$$

$$p_{\mathrm{cm}} = R\ (0.291 - 0.085\omega)\frac{T_{\mathrm{cm}}}{V_{\mathrm{cm}}} \tag{13}$$

$$V_{\mathrm{c}ij} = \frac{1}{8}(V_{\mathrm{c}i}^{\frac{1}{3}} + V_{\mathrm{c}j}^{\frac{1}{3}})^3 \tag{14}$$

$$T_{\mathrm{c}ij} V_{\mathrm{c}ij} = \sqrt{T_{\mathrm{c}i} T_{\mathrm{c}j} V_{\mathrm{c}i} V_{\mathrm{c}j}} \tag{15}$$

3. RESULTS AND DISCUSSION

The linear perturbation (Eq. (8)) and the second-order perturbation models (Eq. (9)), presented in Section 2, were evaluated for the estimation of the speed of sound of pure *n*-alkanes from ethane up to *n*-hexatriacontane, as a function of temperature and pressure. The aim was to select a corresponding-states model able to predict the speed of sound of pure and mixed heavy *n*-alkanes, without requiring any speed-of-sound experimental information from the system under study.

The speed of sound has already been estimated by corresponding-states models [7–9, 42–48], although in most of these studies only simple fluids, such as liquefied gases, refrigerants, and hydrocarbons with chain lengths smaller than *n*-octane were considered.

Using a three-parameter corresponding-states (T, p, ω) model, as presented during the previous section, two different approaches can be found in the literature. In the first one, compressibility factors are directly obtained from the model and other properties, such as the speed of sound, are obtained through thermodynamic relations [7–9]. The second approach is to obtain directly the speed of sound through the expansion of the reduced speed of sound in the Pitzer acentric factor (Eqs. (8) and (9)) [42–48];

$$X_{\mathrm{r}} = u_{\mathrm{r}} = \frac{u \times MW^{1/2}}{T_{\mathrm{c}}^{1/2}} \tag{16}$$

where MW is the molar mass ($\mathrm{g \cdot mol^{-1}}$) [42, 46–48].

More than four thousand experimental liquid phase speeds of sound for *n*-alkanes from ethane up to *n*-hexatriacontane as a function of temperature and pressure were collected from the literature [49–73]. Table I presents an overview of the selected data. Taking into account that large temperature and pressure ranges are involved, the expansion in the reduced speed of sound (Eq. (16)) was adopted, and with this approach, an equation of state that relates the speed of sound with temperature and pressure is required. Daridon and coworkers [9, 60, 68–70, 72–75] have demonstrated that the following function, containing nine adjustable parameters, provide an adequate correlation of speed-of-sound data to within 0.1%, over the available experimental temperature and pressure range.

$$\frac{1}{u^2} = \frac{A_0 + A_1 T_{\mathrm{r}} + A_2 T_{\mathrm{r}}^2 + A_3 T_{\mathrm{r}}^3 + B p_{\mathrm{r}} + C p_{\mathrm{r}}^2 + D p_{\mathrm{r}}^3}{1 + E_1 T_{\mathrm{r}} + F p_{\mathrm{r}}} \tag{17}$$

where A_0–A_3, B, C, D, E_1, and F are adjustable parameters. In this work, for simplicity during the calculation procedure, Eq. (17) is a function of reduced temperature and reduced pressure instead of temperature and pressure, as initially proposed by Daridon and coworkers. Parameters for some *n*-alkanes representing broader temperature and pressure ranges that will be afterwards selected as reference fluids are presented in Table II.

For the purposes of this work, experimental critical properties were used when available [76]. For those *n*-alkanes for which experimental data were unavailable, correlations were used. The critical temperature was obtained from Tsonopoulos correlation [77], the critical pressure from

Table I. Selected *n*-Alkane Speed-of-Sound Data

Alkane	T (K)		p (MPa)		T_r		p_r		Source
	$T_{\min}$	$T_{\max}$	$p_{\min}$	$p_{\max}$	$T_{r\min}$	$T_{r\max}$	$p_{r\min}$	$p_{r\max}$	
C_2H_6	100.0	260.0	3.6	36.8	0.33	1.00	0.73	7.54	[50]
C_3H_8	199.9	340.0	0.0	60.6	0.54	0.92	0.00	14.26	[51]
n-C_4H_{10}	199.8	375.0	0.0	80.4	0.47	0.88	0.00	15.92	[51]
n-C_5H_{12}	263.2	393.2	0.2	208.8	0.56	0.84	0.07	61.97	[52–54]
n-C_6H_{14}	253.0	373.2	0.1	202.7	0.50	0.74	0.03	66.99	[55–60]
n-C_7H_{16}	185.7	523.2	0.0	263.4	0.34	0.97	0.00	96.12	[22, 55, 61, 62]
n-C_8H_{18}	253.2	393.2	0.1	14.0	0.45	0.69	0.04	56.22	[55, 58, 59, 63–66]
n-C_9H_{20}	253.2	413.2	0.1	140.0	0.43	0.69	0.04	61.14	[55]
n-$C_{10}H_{22}$	303.2	413.2	0.1	117.6	0.49	0.67	0.05	55.73	[58, 59, 63, 64, 67]
n-$C_{11}H_{24}$	303.2	413.2	0.1	117.6	0.47	0.65	0.05	59.39	[64]
n-$C_{12}H_{26}$	293.2	473.2	0.1	140.0	0.45	0.72	0.05	76.92	[55, 58, 59]
n-$C_{13}H_{28}$	293.2	373.2	0.1	149.6	0.43	0.55	0.06	89.02	[68]
n-$C_{14}H_{30}$	293.2	373.2	0.1	149.6	0.42	0.54	0.06	95.25	[68]
n-$C_{15}H_{32}$	293.2	383.2	0.1	149.6	0.41	0.54	0.07	101.05	[69]
n-$C_{16}H_{34}$	293.2	453.2	0.1	140.0	0.41	0.63	0.07	100	[55, 67]
n-$C_{17}H_{36}$	303.2	383.2	0.1	149.6	0.41	0.52	0.07	101.60	[69]
n-$C_{18}H_{38}$	313.2	383.2	0.1	149.6	0.42	0.51	0.08	115.93	[70]
n-$C_{19}H_{40}$	313.2	383.2	0.1	149.6	0.41	0.51	0.09	128.92	[70]
n-$C_{20}H_{42}$	323.2	393.2	0.1	149.6	0.42	0.51	0.09	139.77	[71]
n-$C_{22}H_{46}$	323.2	393.2	0.1	149.6	0.41	0.50	0.10	152.60	[71]
n-$C_{23}H_{48}$	333.2	393.2	0.1	149.6	0.42	0.50	0.11	162.55	[72]
n-$C_{24}H_{50}$	333.2	393.5	0.1	149.6	0.42	0.49	0.11	171.90	[72]
n-$C_{28}H_{58}$	353.15	403.15	0.10	149.55	0.43	0.49	0.14	205.42	[73]
n-$C_{32}H_{66}$	353.15	403.15	0.10	150.00	0.41	0.47	0.02	251.03	[17]
n-$C_{36}H_{74}$	363.15	403.15	0.10	151.30	0.42	0.46	0.20	305.55	[73]

Magoulas and Tassios [78], the critical volume from Marano and Holder [79], and the Pitzer acentric factor from Han and Peng [80]. Arguments for selecting these correlations were presented elsewhere [81].

In previous studies it was shown that for *n*-alkanes, the reduced vapor–liquid interfacial tension, liquid density, viscosity, vapor pressure, and thermal conductivity [10, 11, 13, 14] are not linear with the acentric factor, but instead show a weak quadratic dependence. It was also shown that the introduction of the second-order term improved considerably the results in a broad temperature range. In the case of speed of sound, and as can be seen from Table I, the available data for the heavier *n*-alkanes are within a very narrow reduced temperature range, and thus a full temperature scan cannot be performed as done before. The reduced speed of sound as a function of acentric factor at $T_r = 0.4$ and atmospheric pressure is plotted in Fig. 1 for *n*-alkanes from C_2H_6 up to n-$C_{36}H_{74}$. C_3H_8,

Table II. Correlating Coefficients of the Reference Fluids to be Used with Eq. (17)

n-Alkane	$A_0 \times 10^7$	$A_1 \times 10^6$	$A_2 \times 10^6$	$A_3 \times 10^6$	$B \times 10^8$	$C \times 10^{11}$	$D \times 10^{13}$	E_1	$F \times 10^2$
n-C_6H_{14}	−2.146	2.099	−3.258	2.278	1.363	−21.66	17.57	−1.003	3.660
n-C_7H_{16}	3.992	−1.437	3.475	−2.063	0.713	−7.042	3.520	−1.075	2.527
n-$C_{15}H_{32}$	−7.939	5.762	−10.52	7.238	0.389	−2.325	0.824	−1.088	1.402
n-$C_{16}H_{34}$	−13.60	8.832	−15.86	10.28	0.517	−3.289	1.199	−1.078	1.569
n-$C_{24}H_{50}$	−8.405	6.300	−11.89	8.434	0.192	−0.701	0.159	−1.103	0.755

n-C_5H_{12}, and n-C_6H_{14} are not included in this plot as data were only reported for reduced temperatures above $T_r = 0.5$, as shown in Table I.

In this case, the reduced property is practically linear with the acentric factor, which suggests that the introduction of the second-order term should not significantly improve the results, as will be demonstrated below.

In order to use the models presented in Section 2 for speed of sound, two (Eq. (8)) or three (Eq. (9)) reference fluids are required. These should provide adequate estimates of speed of sound as a function of temperature and pressure. It was previously shown that the simultaneous selection of lighter and heavier components for reference fluids provided the best results [10, 11, 13, 14]. For this reason, n-C_6H_{14}, n-C_7H_{16}, n-$C_{15}H_{32}$, n-$C_{16}H_{34}$, and n-$C_{24}H_{50}$ were selected as candidates for reference fluids, as they presented the broader temperature and pressure ranges of available data, and thus, low risk of extrapolation of the speed-of-sound correlating equations.

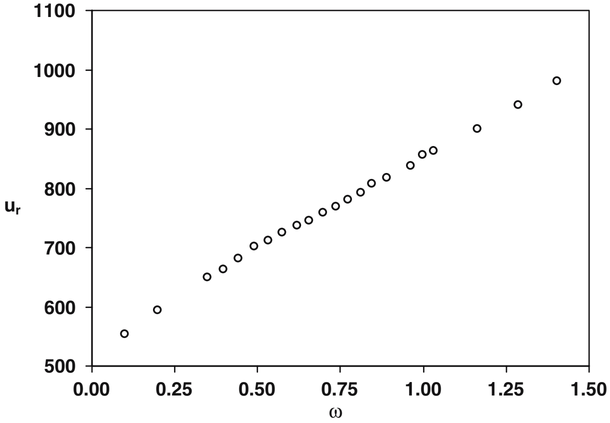

Fig. 1. Reduced speed of sound as a function of the acentric factor (ω) at $T_r = 0.4$.

Results using different combinations of the proposed reference fluids are presented in Table III. As can be seen, the best average deviations are obtained with the linear perturbation model using n-C_7H_{16} + n-$C_{24}H_{50}$ as a reference system, but in the case of this model, the average deviation is reference system dependent. Using another combination of reference fluids, the average deviation can increase up to 8%. With the second-order perturbation model the average deviations are more independent of the reference system, with a maximum difference among different reference systems below 1%. The best estimates with this approach were obtained using n-C_7H_{16} + n-$C_{16}H_{34}$ + n-$C_{24}H_{50}$ as a reference system.

Pure component results obtained with the best sets of reference systems are reported in Table IV. More than 4000 experimental values of speed of sound were predicted. In both cases, the average absolute percent deviations (AAD %) are less than 2%. Larger deviations are obtained, in both cases for the lighter elements of the series (Fig. 2). These are due to their broader reduced temperature and pressure ranges, as can be verified in Table I and in Fig. 3 for propane. This requires extrapolation of the reference fluid equations (Eq. (17)), which in this study showed poor extrapolation capacities. This can also be confirmed in Fig. 4, where the average absolute percent deviation is plotted as a function of temperature and pressure for n-$C_{28}H_{58}$. It can be seen that with the exception of the high-temperature, and especially the high-pressure region, deviations are very small, below 1%. The same happens for most of the other n-alkanes whose data are within the reduced temperature and reduced pressure ranges of the data used to perform the parameter fitting in Eq. (17). This suggests that additional reference fluid data or some constraint imposition

Table III. Evaluation of Reference Systems

Model	Reference system	AAD (%)
Linear perturbation (Eq. (8))	n-C_6H_{14} + n-$C_{15}H_{32}$	7.5
	n-C_6H_{14} + n-$C_{16}H_{34}$	5.8
	n-C_6H_{14} + n-$C_{24}H_{50}$	3.2
	n-C_7H_{16} + n-$C_{15}H_{32}$	3.0
	n-C_7H_{16} + n-$C_{16}H_{34}$	2.1
	n-C_7H_{16} + n-$C_{24}H_{50}$	1.6
	n-$C_{15}H_{32}$ + n-$C_{24}H_{50}$	3.0
	n-$C_{16}H_{34}$ + n-$C_{24}H_{50}$	2.8
2nd-order perturbation (Eq. (9))	n-C_6H_{14} + n-$C_{15}H_{32}$ + n-$C_{24}H_{50}$	2.8
	n-C_6H_{14} + n-$C_{16}H_{34}$ + n-$C_{24}H_{50}$	2.2
	n-C_7H_{16} + n-$C_{15}H_{32}$ + n-$C_{24}H_{50}$	2.1
	n-C_7H_{16} + n-$C_{16}H_{34}$ + n-$C_{24}H_{50}$	1.8

Table IV. Pure *n*-Alkane Corresponding-States Results

n-Alkane	AAD (%) Linear perturbation	AAD (%) 2nd-order perturbation	Number of data points
C_2H_6	2.1	8.0	66
C_3H_8	2.0	9.4	241
n-C_4H_{10}	1.2	4.4	249
n-C_5H_{12}	6.0	7.7	257
n-C_6H_{14}	0.72	1.2	404
n-C_7H_{16}	0.20	0.20	452
n-C_8H_{18}	1.1	1.2	330
n-C_9H_{20}	0.42	0.58	89
n-$C_{10}H_{22}$	0.53	0.88	215
n-$C_{11}H_{24}$	0.76	1.0	91
n-$C_{12}H_{26}$	1.3	1.8	83
n-$C_{13}H_{28}$	0.31	0.18	276
n-$C_{14}H_{30}$	0.26	0.14	251
n-$C_{15}H_{32}$	0.41	0.07	142
n-$C_{16}H_{34}$	0.68	0.51	152
n-$C_{17}H_{36}$	0.66	0.22	124
n-$C_{18}H_{38}$	0.93	0.53	141
n-$C_{19}H_{40}$	0.69	0.29	134
n-$C_{20}H_{42}$	0.62	0.70	113
n-$C_{22}H_{46}$	0.42	0.29	104
n-$C_{23}H_{48}$	0.52	0.28	97
n-$C_{24}H_{50}$	0.07	0.07	92
n-$C_{28}H_{58}$	1.3	1.1	87
n-$C_{32}H_{66}$	4.2	1.9	85
n-$C_{36}H_{74}$	8.7	4.8	64
Average	1.6	1.8	Total = 4339

should be included during the parameter fitting procedure, in order to improve the results at high temperature and/or high pressure.

Results for four *n*-alkane binary mixtures as a function of temperature and pressure are reported in Table V. As can be seen, very good agreement with the experimental data, on average, less than 2%, was obtained, showing that the corresponding-states principle may be an excellent tool for estimation of the speed of sound of both pure and mixed fluids in a broad range of thermodynamic conditions.

4. CONCLUSION

Two corresponding-states models based on a Taylor series expansion of the reduced evaluating property on the Pitzer acentric factor were

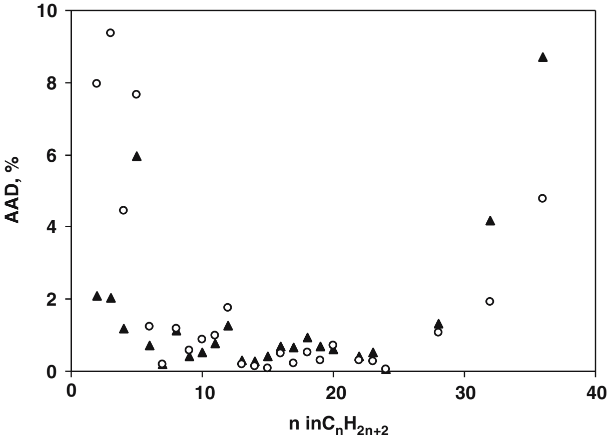

Fig. 2. Average absolute percent deviations as a function of chain length, using the best sets of reference systems: ▲, linear perturbation; ○, 2nd-order perturbation.

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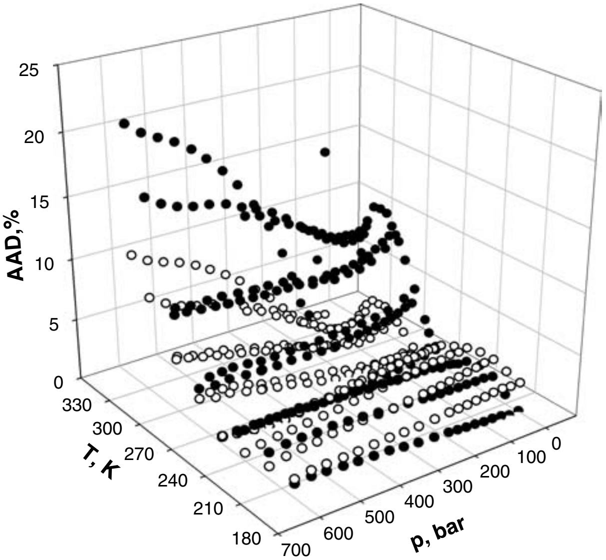

Fig. 3. Average absolute percent deviations for n-C_3H_8: ○, linear perturbation; ●, 2nd-order perturbation.

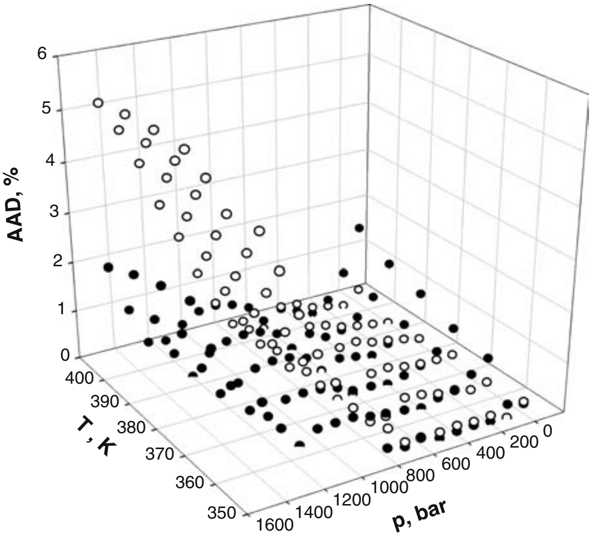

Fig. 4. Average absolute percent deviations for n-$C_{28}H_{58}$: ○, linear perturbation; •, 2nd-order perturbation.

Table V. Corresponding-States Results for Binary n-Alkane Mixtures

Mixture	AAD (%) Linear perturbation	AAD (%) 2nd order perturbation	Number of data points	Source
n-C_6H_{14} + n-$C_{10}H_{22}$	0.71	0.86	15	[59]
n-C_6H_{14} + n-$C_{16}H_{34}$	1.80	2.02	346	[82]
n-C_8H_{18} + n-$C_{12}H_{26}$	0.51	1.04	15	[59]
n-$C_{10}H_{22}$ + n-$C_{14}H_{30}$	0.28	0.76	15	[59]
Average (all points)	1.66	1.89		

extended for the estimation of the available n-alkane speed-of-sound data as a function of temperature and pressure. Small average deviations, less than 2% were obtained in both cases, but higher deviations resulted for those n-alkanes presenting high reduced temperature and/or reduced pressure data, showing that either new data should be included or consistency constraints shall be considered in order to obtain better extrapolation ability, and thus increase the ability to estimate the speed of sound at any set of conditions. At this point it is expected that estimations may be obtained with deviations around 1%, and thus very close to the experimental uncertainties.

The application of this model for mixtures is straightforward given the pure component critical properties and Pitzer acentric factors. The results obtained suggest that this model should be a reliable tool for estimation of the speed of sound of mixtures containing different *n*-alkanes.

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