Experimental speed of sound in CO_2-rich mixtures with methanol. Extrapolation to pure CO_2

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High pressure speed of sound apparatus

Double-path double-echo pulsed ultrasonic system

253 K – 473 K   *u*(*T*)=0.015 K

0.1 MPa – 200 MPa   *u*(*P*)=0.02 MPa

Frequency: 5 MHz

At 5 MHz

Pure CO_2 → no signal

CO_2-rich mixtures of interest for CCS, → poor or no signal

C. W. Lin, PhD Thesis, 2013

Pure CO_2: No signal at 2 MHz

Partial success at 0.5 MHz

C.W. Lin, PhD Thesis, 2013

C.W. Lin and J.P.M. Trusler, 2014, J. Chem. Eng. Data, 59, 4099-4109

Doping CO_2 with small amounts of propane at 2 MHz

Good signals

Successful extrapolation to pure CO_2

At 5 MHz

CO_2 + propane is opaque for x_{CO_2}>0.8 (approx.)

In our study CO_2+SO_2

We hoped

SO_2 itself could act as doping agent in the CO_2+SO_2 mixtures

BUT

It only works at $x_{\mathrm{CO_2}} \leq 0.9$

At $x_{\mathrm{CO_2}}=0.95$:

very poor signals along very short ranges of pressure and only at low temperatures

LOOKING FOR A SUITABLE DOPING AGENT

Methanol

- **reduces significantly the sound absorption coefficient of the mixture**
- **works well until x_{CO_2} ≈0.99 in a CO_2+CH_3OH mixture**
- **can appear in the CCS facilities**
  - ✓ **impurity in anthropogenic CO_2**
  - ✓ **used to avoid hydrates formation**
  - ✓ **a residue from pipeline drying**

Experimental speed of sound in CO_2-rich mixtures with methanol. Extrapolation to pure CO_2

Aim of this work

To test the suitability of methanol as doping agent, in order to obtain good measurements of speed of sound in CO_2 at 5 MHz and, in the future, in CO_2-rich mixtures of interest for CCS.

To evaluate the doping effect.

Experimental speed of sound in CO_2-rich mixtures with methanol. Extrapolation to pure CO_2

For this purpose

- We measured the speed of sound in seven CO_2-rich mixtures with methanol at several *P* and *T* and at 5 MHz
- We obtained extrapolated values of *c* in pure CO_2
- We evaluated the effect of the doping on *c* by comparing our results with the Span and Wagner EoS
- We used the experimental results for the mixtures to validate the PC-SAFT and the GERG EoSs

Measuring of the speed of sound, *c*, in seven mixtures CO_2+CH_3OH

COMPOSITIONS
x_{CO_2}
0.8005
0.9025
0.9503
0.9700*
0.9794
0.9845
0.9898

TEMPERATURES (K)
263.15
298.15
323.15

PRESSURES (MPa)
3-200

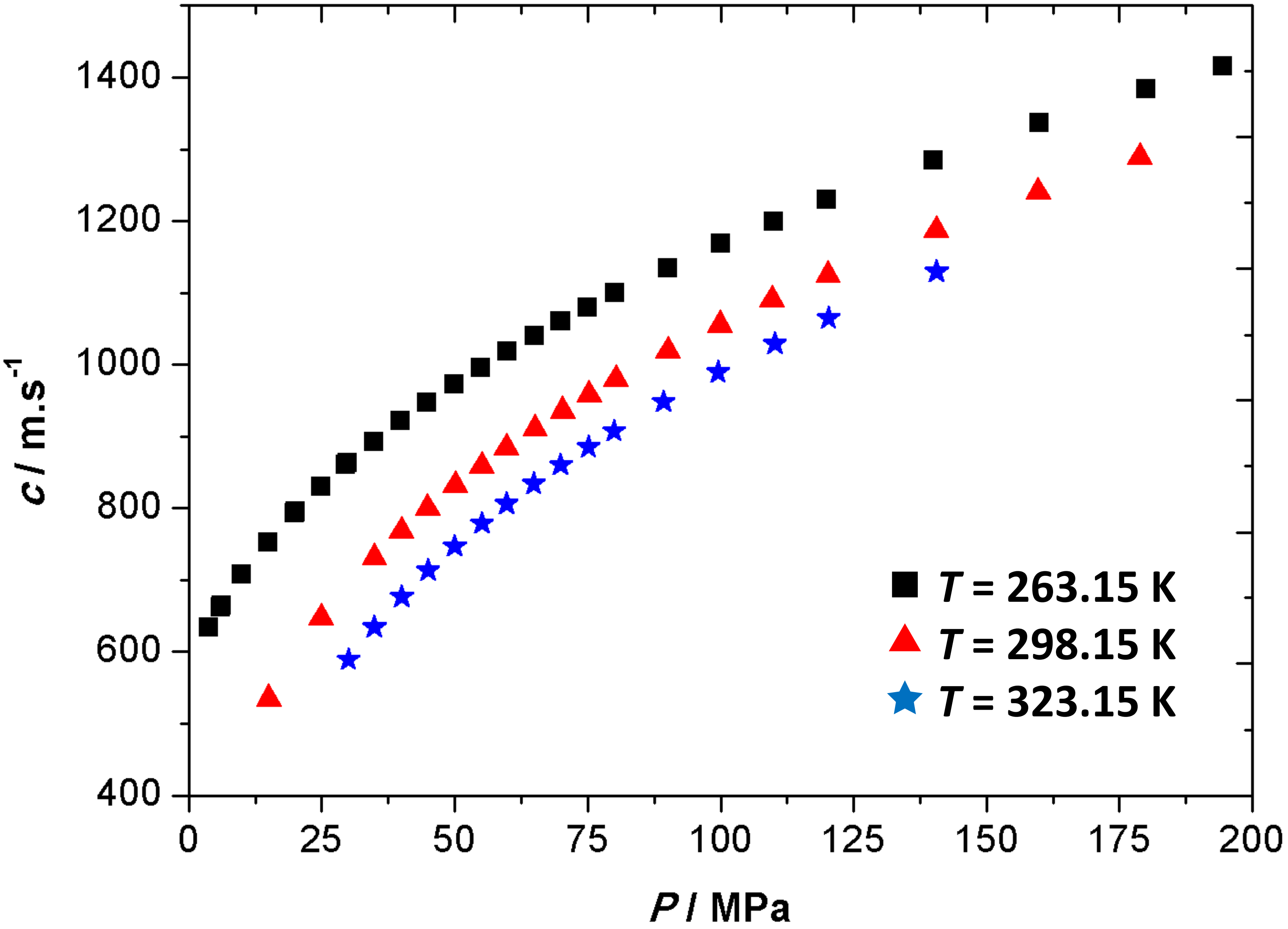
$u(c)$=0.059%

Used for the extrapolation to pure CO_2 ⇒ Compared with the Span and Wagner EoS

All the isotherms were used for PC-SAFT and GERG EoS validation

*At 263.15 K, Rivas, C., Gimeno, B., Bravo, R., Artal, M., Fernández, J., Blanco, S.T., Velasco,I., 2nd International Forum on Recent Developments of CCS Implementation, Athens 2015.

Experimental speeds of sound, *c*, in the CO_2+CH_3OH mixture with x_{CO_2} =0.9503.



With the experimental results of the five most concentrated mixtures

COMPOSITIONS
x_{CO_2}
0.8005
0.9025
0.9503
0.9700
0.9794
0.9845
0.9898

TEMPERATURES (K)
263.15
298.15
323.15

PRESSURES (MPa)
3-200

EXTRAPOLATION TO PURE CO_2

The experimental results of each isotherm an isopleth were fitted to a polinomial:

$$(P - P^{\#}) = a_1(c - c^{\#})^1 + a_2(c - c^{\#})^2 + a_3(c - c^{\#})^3 \qquad (1)$$

$P^{\#}$ =70 MPa; $c^{\#}$ = c at $P^{\#}$

Coefficients of the equation 1 for the mixture CO_2 + CH_3OH with x_{CO_2} = 0.9503 at temperatures *T*, and mean relative deviations.

x_{CO_2}	T/K	$10 \times a_1$ MPa.m^{-1}.s	$10^4 \times a_2$ MPa.m^{-2}.s^2	$10^8 \times a_3$ MPa.m^{-3}.s^3	MRD_c %
0.9503	263.15	2.5039	2.543	7.33	0.019
	298.15	2.1649	2.271	7.40	0.012
	323.15	2.0001	2.127	7.10	0.004

$$MRD_c(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{c_{i,fit} - c_i}{c_i}\right|$$

From the polynomials (1), we obtained values of *c* at round values of *P* at each *T* and at each composition

These values of *c*, at each *T* and at each round *P*, for the five studied compositions, were fitted to

$$c(x_{CO_2}) = c_0 + c_1(1 - x_{CO_2}) + c_2(1 - x_{CO_2})^2 \qquad (2)$$

c_0 is the speed of sound at a given *T* and at a given round value of *P* for $x_{CO_2} = 1$

c_0 is the extrapolated speed of sound in pure CO_2 at *T* and *P*

Average overall uncertainty 0.12%

That way, we obtained the extrapolated speeds of sound in pure CO_2 at each given *T* and round *P*

Derived *c* in pure CO_2: comparison with the literature and the S-W EoS

Reference	**Type of data**	***MRD_c*(%)**
Pitevskaya and Bilevich, 1973	Direct experimental	0.61%*
Al-Siyabi, 2013	Direct experimental	Consistent**
Lin, 2014	Direct experimental at 0.5 MHz	0.44%*
Lin and Trusler, 2014	Derived with propane at 2 MHz	0.21%*
Span and Wagner, 1996	**Equation of state**	**0.43%***
Tolerance margin of the S-W EoS	**0.5%-2%**	

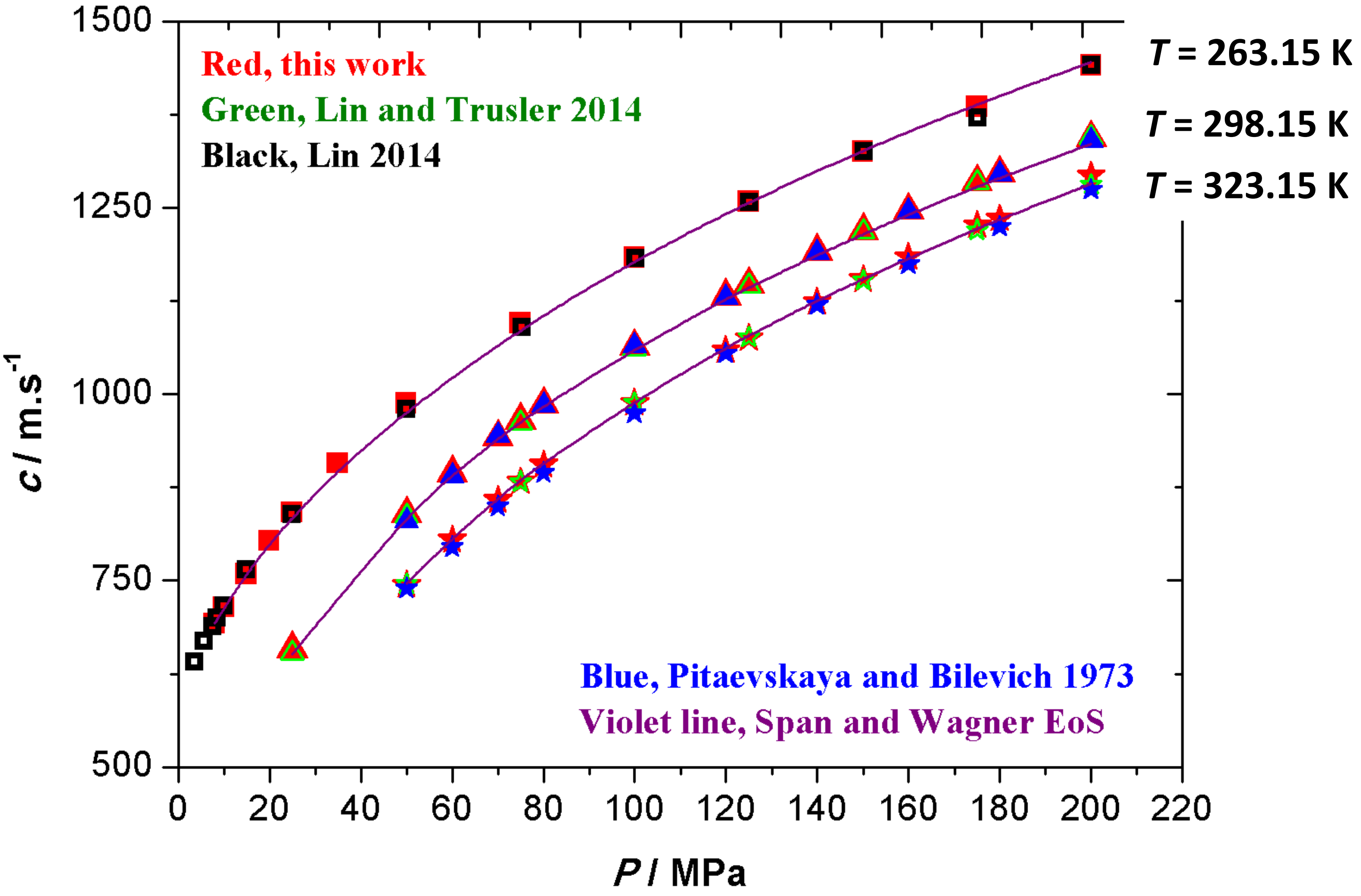
*At the common temperatures

**Temperatures were different

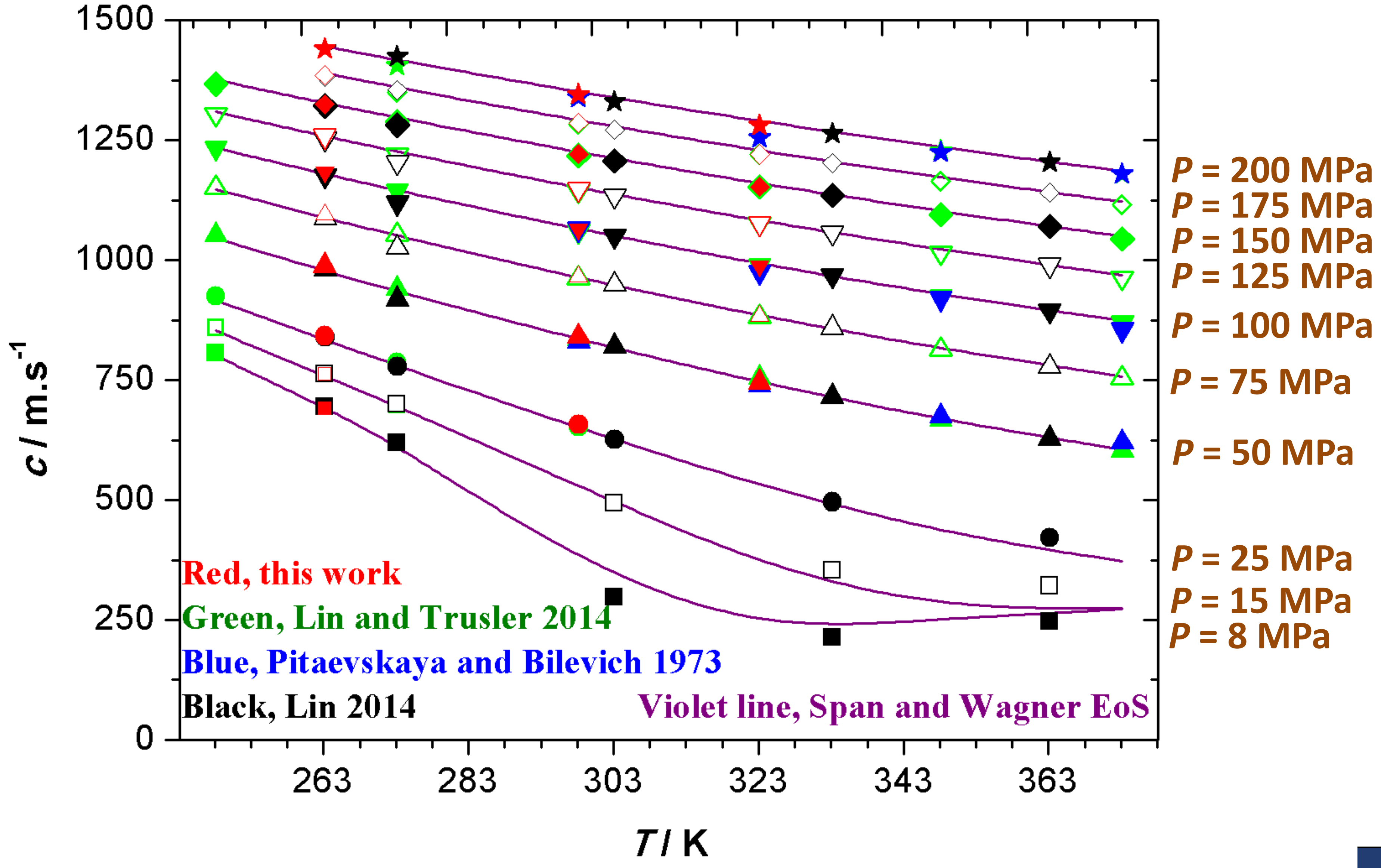
$$MRD_c(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{c_{i,lit} - c_i}{c_i}\right|$$

The deviations are higher than the uncertainty of our *c* in pure CO_2, (0.12%), but lower than the tolerance margin of the Span and Wagner EoS

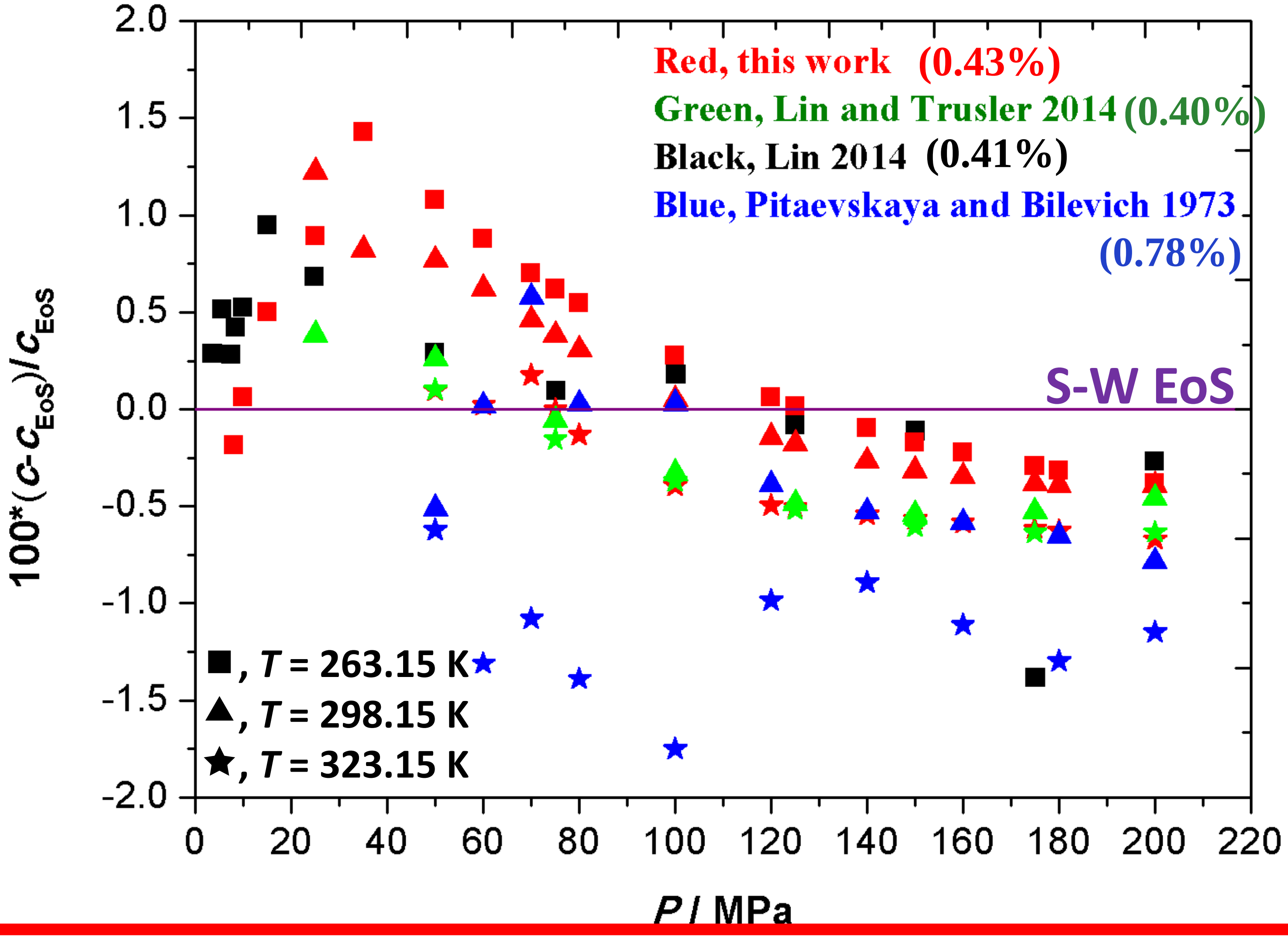
Speed of sound, c, in pure CO_2 versus pressure, *P*.



Speed of sound, *c*, in pure CO_2 versus temperature, *T*.



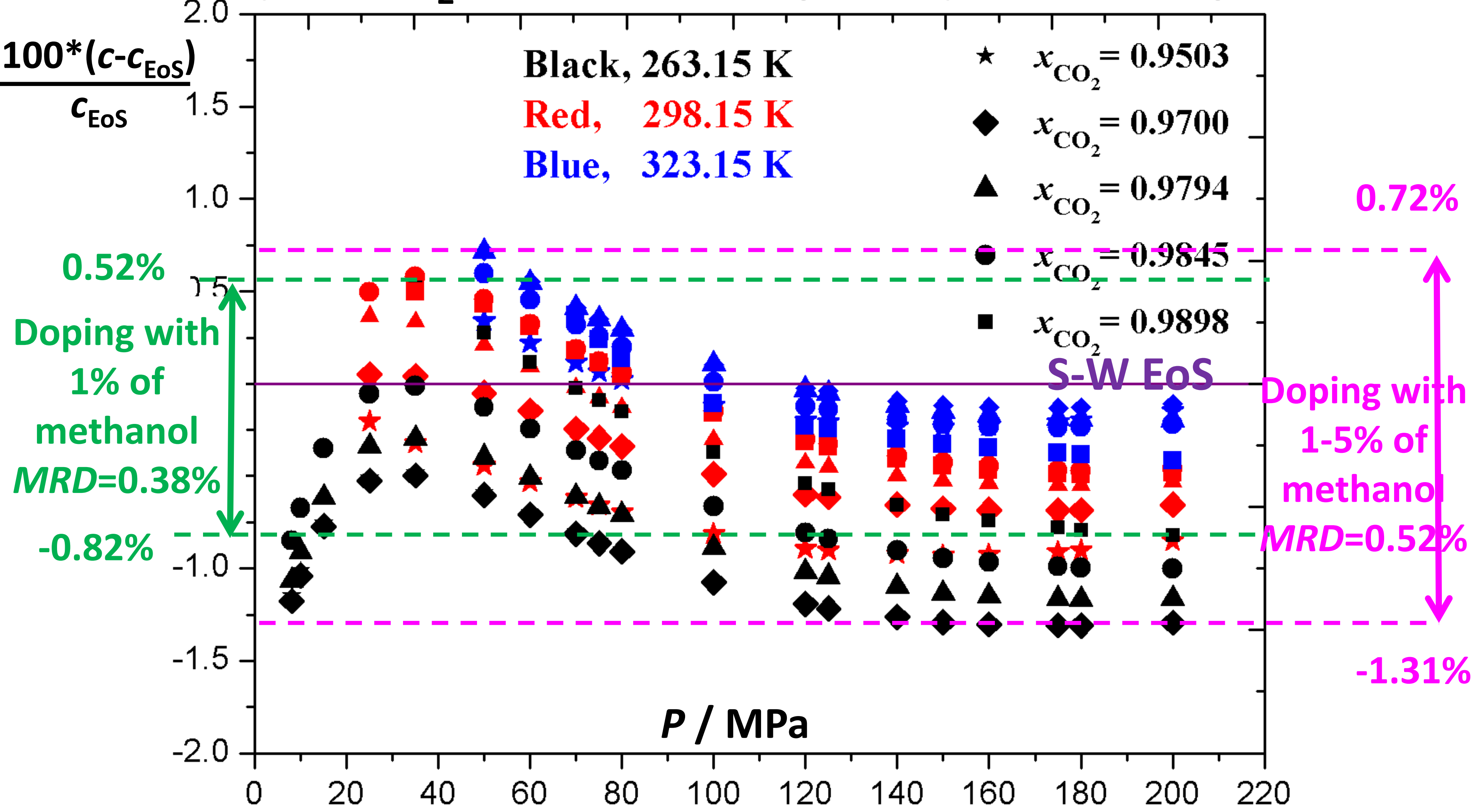
Relative deviations of *c* in pure CO_2 from the Span and Wagner EoS



LAST THREE FIGURES:

Good agreement of the whole set of data and the Span and Wagner EoS

Relative deviations of our *c* in the mixtures CO_2+CH_3OH from those in pure CO_2 calculated using the Span and Wagner EoS.



0.52%

Doping with 1% of methanol *MRD*=0.38%

-0.82%

0.72%

Doping with 1-5% of methanol *MRD*=0.52%

-1.31%

The deviations are higher than the experimental uncertainty (0.059%), but they are almost always inside the tolerance margin of the Span and Wagner EoS (0.5-2%)

COMPARISON WITH EoSs

OUR EXPERIMENTAL SPEEDS OF SOUND FOR ALL THE CO_2+CH_3OH MIXTURES

-

PC-SAFT AND GERG EoSs

PC-SAFT EoS applied to CO_2+CH_3OH

$$\tilde{a} = \tilde{a}^{id} + \tilde{a}^{hc} + \tilde{a}^{dis} + \tilde{a}^{assoc} + \left(\tilde{a}^{QQ} + \tilde{a}^{DD} + \tilde{a}^{QD}\right)$$

- **For pure compounds m; σ; and ε calculated from the pure compounds' critical temperatures and pressures (Gil et al., 2012)*.**

- **The mixing parameters σ_{ij} and ε_{ij} :**

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right) \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right)$$

$$k_{ij} = -0.323 + 2.88 \times 10^{-4}\ T$$

(*) Gil, L. et al., 2012. The Journal of Supercritical Fluids, 71, 26-44.

PC-SAFT EoS applied to CO_2+methanol

non-self-association
CO_2

self-association compound
Methanol

INDUCED ASSOCIATION*:

- The association volume, $\kappa^{A_iB_i}$=$\kappa^{methanol}$, and the association energy, $\varepsilon^{A_iB_i}$= 0 for CO_2 with a 2C association scheme.
- The association volume, $\kappa^{A_iB_i}$, and the association energy, $\varepsilon^{A_iB_i}$ for methanol with a 2B association scheme.
- The **cross-association** parameters, $\kappa^{A_iB_j}$= $\kappa^{methanol}$, and $\varepsilon^{A_iB_j}$= $\kappa^{methanol}$/2.

(*) Kleiner, M., Sadowski, G., 2007. The Journal of Physical Chemistry C, 111, 15544-15553.

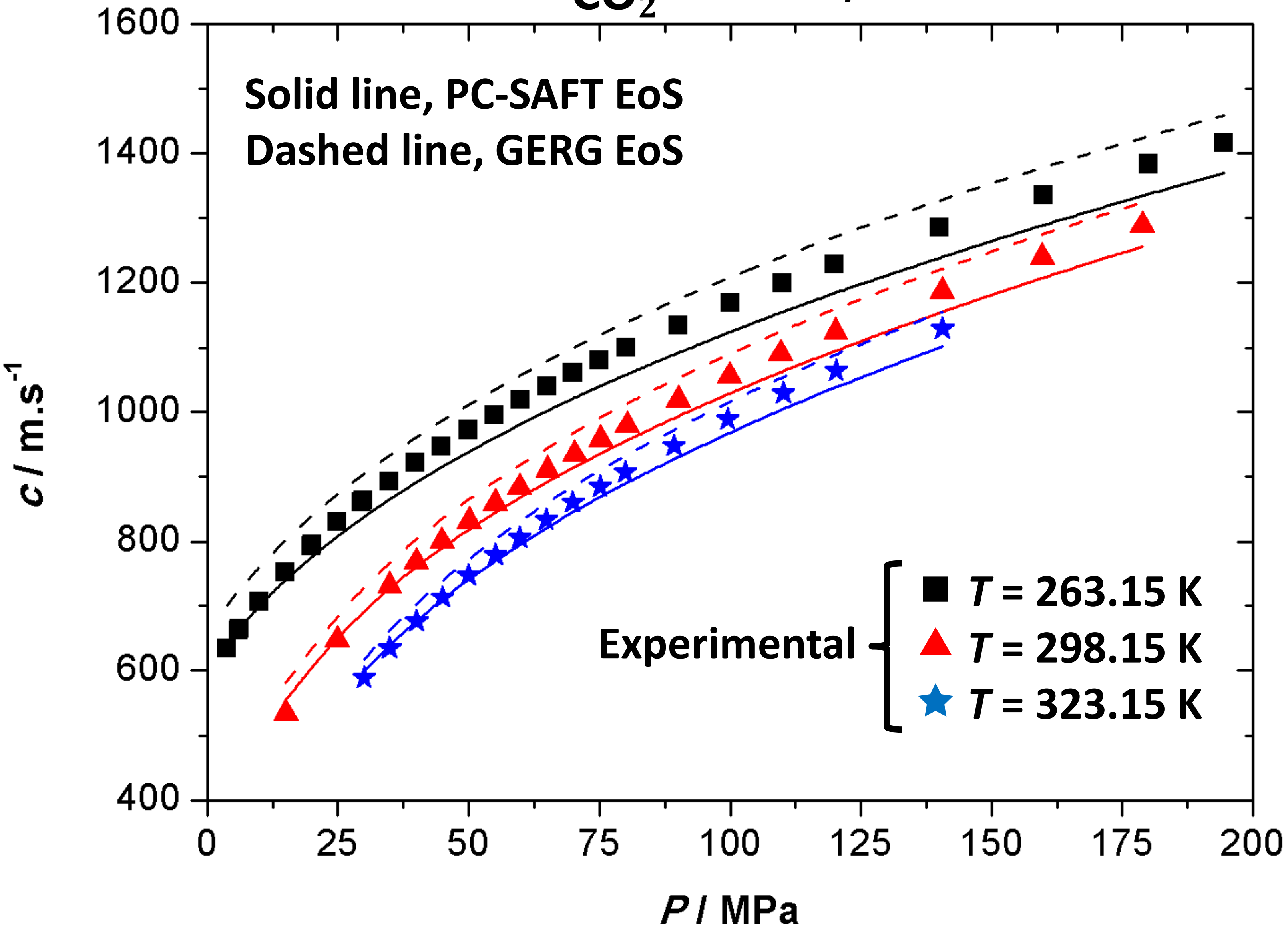
GERG EoS applied to CO_2+CH_3OH

$$\tilde{a} = \tilde{a}^{id} + \tilde{a}^{res} = \sum_{i=1}^{N} x_i\left[\tilde{a}_i^{id} + \ln x_i\right] + \sum_{i=1}^{N} x_i\tilde{a}_i^{res} + \Delta\tilde{a}^{res}$$

- Although methanol is not one of the 21 compounds included in the Kunz and Wagner article (Kunz and Wagner, 2012), it has been implemented in the used **REFPROP 9** software.

(*) Kunz, O., Wagner, W., 2012. The Journal of Chemical & Engineering Data, 57, 3032-3091.

Speeds of sound, *c*, in the CO_2+CH_3OH mixture with x_{CO_2}=0.9503,



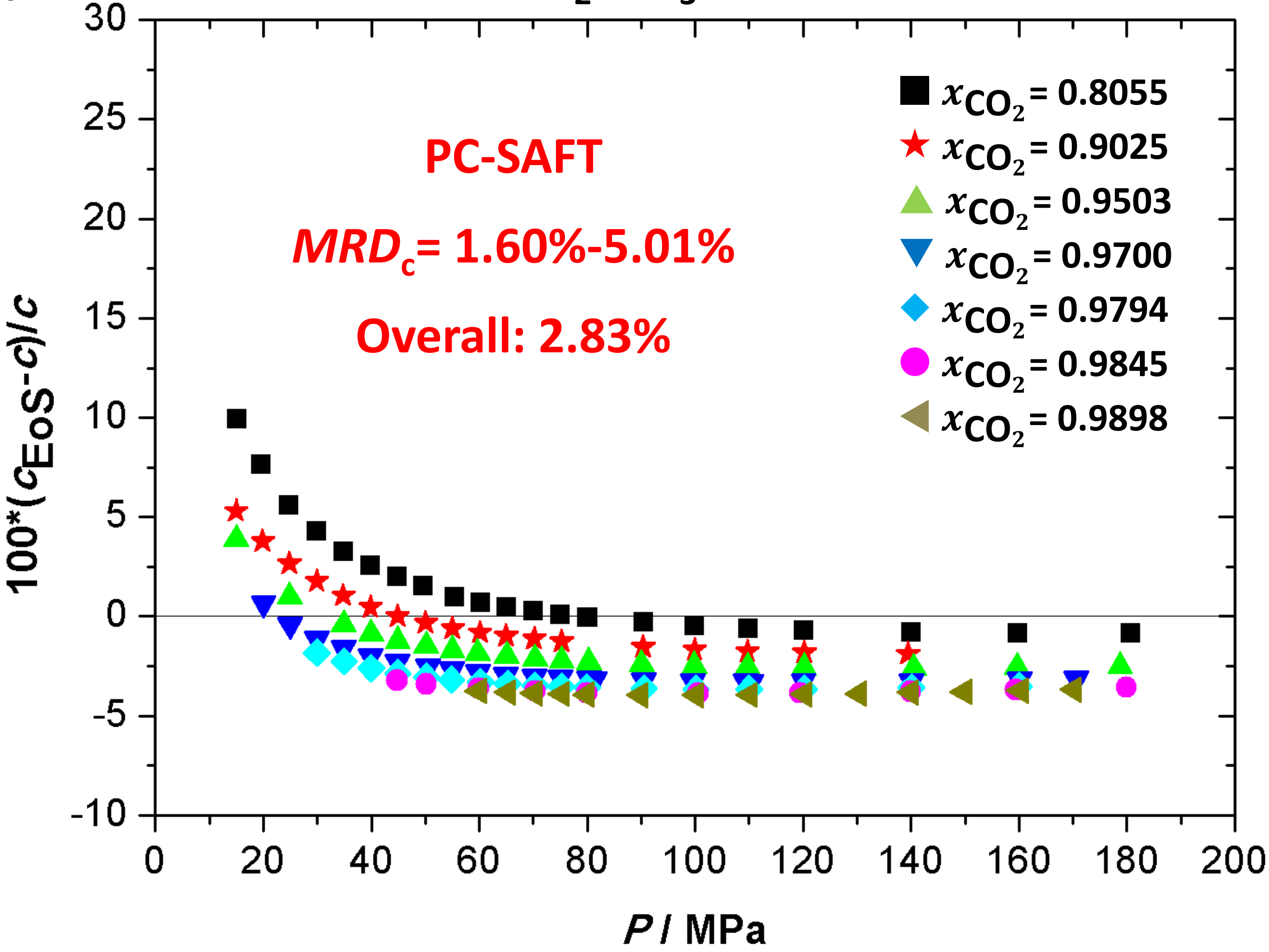
		$MRD_c(\%)$ $T = 263.15$ K			$MRD_c(\%)$ $T = 298.15$ K			$MRD_c(\%)$ $T = 323.15$ K	
x_{CO_2}		PC-SAFT	GERG		PC-SAFT	GERG		PC-SAFT	GERG
0.8005		2.12	11.7		2.09	12.9		2.16	11.0
0.9025		2.56	7.12		1.60	7.65		1.57	6.49
0.9503		2.82	4.95		2.05	4.23		1.55	3.16
0.9700		3.08	3.62		2.61	2.29		2.56	1.40
0.9794		3.98	2.15		3.22	1.34		2.95	0.86
0.9845		4.32	1.55		3.66	0.85		3.09	0.74
0.9898		5.01	0.80		3.86	0.64		3.15	0.65

	$MRD_c(\%)$	
	PC-SAFT	GERG
overall	**2.83**	**4.97**
x_{CO_2}≥0.98	**3.69**	**1.06**

$$MRD_c(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{c_{i,\mathrm{EoS}} - c_i}{c_i}\right|$$

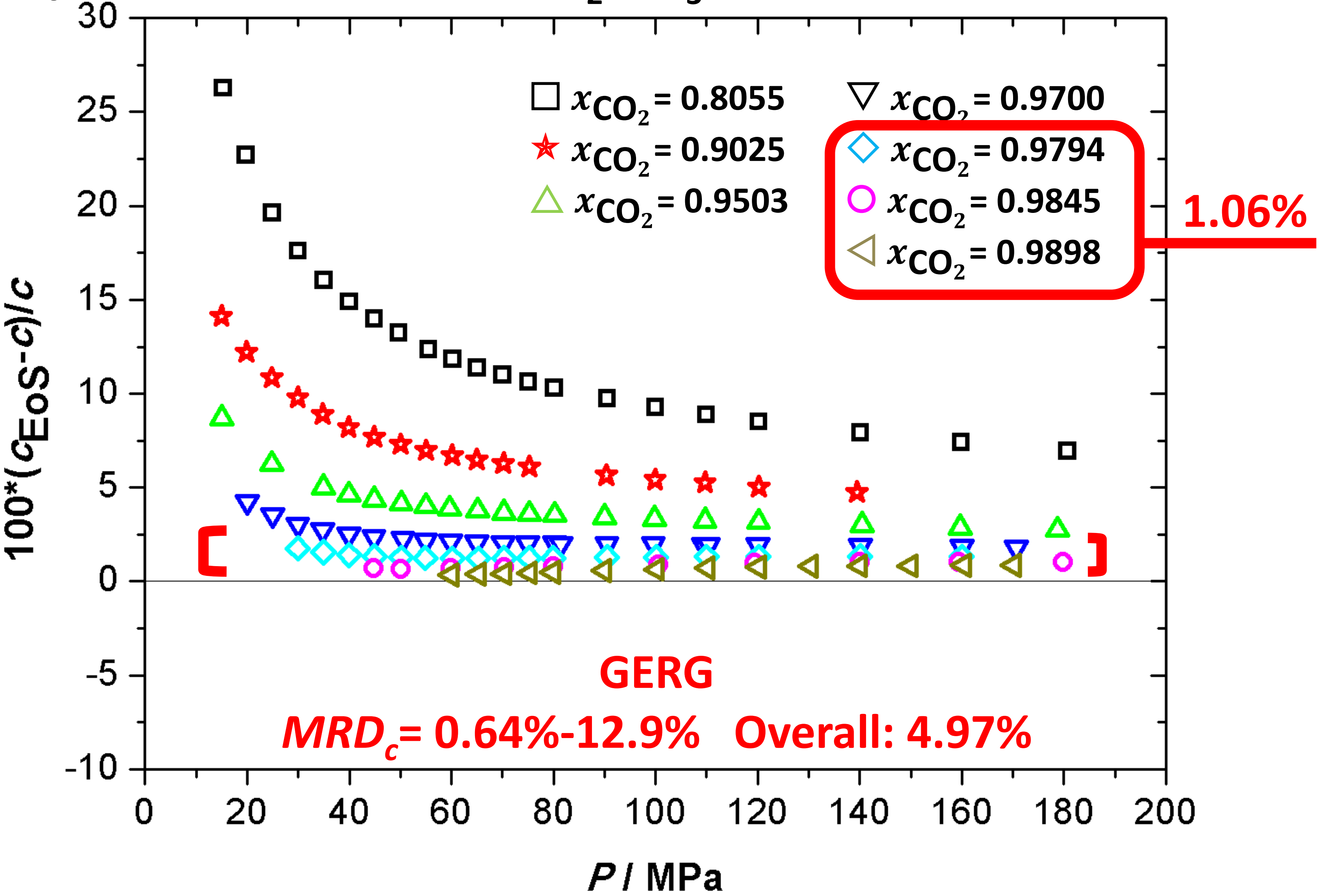
COMPARISON EXPERIMENTAL - PC-SAFT

Speeds of sound for the CO_2+CH_3OH mixtures at T = 298.15 K



COMPARISON EXPERIMENTAL - GERG

Speeds of sound for the CO_2+CH_3OH mixtures at T = 298.15 K



1.06%

GERG

***MRD$_c$*= 0.64%-12.9% Overall: 4.97%**

CONCLUSIONS

Acoustic measurements are needed for CCS

Great difficulties to determine the speed of sound in pure CO_2 and in CO_2 -rich mixtures at high pressures.

Doping with methanol ⟹ good measures of *c* in CO_2 at 5 MHz

The effect of the doping has been quantified.

The PC-SAFT and GERG EoS have been validated with the exception of GERG for the methanol-richest mixtures.

NEXT STEP

To extend this method to opaque CO_2-rich mixtures of interest for CCS technology.

Speeds of sound in CO_2 + SO_2 mixtures doping with 0.8% of methanol

x_{SO_2} = 0.103

Without methanol

undoped

x_{CO_2} = 0.8969

x_{SO_2} = 0.1031

u_c = 0.06%

with methanol

doped

x_{CO_2} = 0.8888

x_{CH_3OH} = 0.0080

x_{SO_2} = 0.1032

$\left.\begin{array}{l} x_{CO_2} = 0.8888 \\ x_{CH_3OH} = 0.0080 \end{array}\right\}$ $x_{solvent}$ = 0.8968

u_c = 0.09%

Differences (MRD_c)

doped-undoped

$\left\{\begin{array}{l} 0.20\% \text{ at } 263.15\text{ K} \\ 0.14\% \text{ at } 293.15\text{ K} \\ 0.15\% \text{ at } 353.15\text{ K} \end{array}\right.$ → $\overline{MRD_c}$ = 0.16%

COMPARISON

CO_2+SO_2 UNDOPED MIXTURE

CO_2+SO_2 DOPED MIXTURE

PC-SAFT

GERG

GERG: REFPROP 9

PC-SAFT: Binary mixture

Parameter	Reference
CO_2	Gross-Sadowski, 2001
SO_2	Gross-Sadowski, 2001
k_{ij} (CO_2-SO_2)= 0.03	Diamantonis, 2013

PCSAFT: Ternary mixture

Parameter	Reference
CO_2 (ASSO.2C)	Gil et al., 2012
SO_2	Gross-Sadowski, 2001
CH_3OH (ASSO.2B)	Gil et al., 2012
k_{ij} (CO_2-SO_2)= 0.03 $k_{ij}(\mathrm{CO_2}-\mathrm{CH_3OH}) = -0.323 + 2.88 \times 10^{-4}\ T$ $k_{ij}(\mathrm{SO_2}-\mathrm{CH_3OH}) = 0$	Diamantonis, 2013 Gil et al., 2012

COMPARISON **EXP. UNDOPED** / **EXP. DOPED** ⟷ **PC-SAFT** / **GERG** **(T = 263.15 K, 293.15 K, 353.15 K)**

MRD_c(%)	EoS →	<u>undoped mixture</u> CO_2(0.8969) + SO_2(0.1031)	<u>doped mixture</u> CO_2(0.8888) + SO_2(0.1032) + CH_3OH(0.080)
EXPERIMENTAL ↓			
<u>undoped mixture</u> CO_2(0.8969) + SO_2(0.1031)		PC-SAFT 2.20% GERG 1.77%	PC-SAFT 4.30% GERG 1.58%
<u>doped mixture</u> CO_2(0.8888) + SO_2(0.1032)+ CH_3OH(0.080)		PC-SAFT 2.44% GERG 1.23%	PC-SAFT 3.72% GERG 1.26%

$$MRD_c(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{c_{i,\mathrm{EoS}} - c_i}{c_i}\right|$$

CONCLUSION

Differences doped - undoped (0.16%)

little higher than experimental uncertainty (0.09%)

much lower than deviations from the PC-SAFT and GERG EoSs (1.23-4.40%)

The effect of methanol in the speed of sound values is quite small for the experiments and negligible for modelling

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Thank you for your attention

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