Using volume shifts to improve the description of speed of sound and other derivative properties with cubic Equations of State.

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Supplementary Data

Table A1 – Pure compound parameters using the modified EoS parameterizations.

Compound	a_c (Pa.m^6.mol^{-2})	$b.\ 10^5$ (m^3.mol^{-1})	c_1	c_2	c_3	c_4	c_5	$\beta.10^2$	ε (J.mol^{-1})
hexane (SRK)	2.53	12.12	1.06	-2.01	12.02	-33.1	35.1		
hexane (PR)	2.70	10.88	0.88	-1.38	9.61	-27.6	29.9		
decane (SRK)	5.32	21.00	1.41	-3.73	28.05	-102.9	148.3		
decane (PR)	5.69	18.85	1.20	-2.77	22.89	-85.7	124.3		
hexadecane (SRK)	10.93	36.89	1.90	-6.28	43.88	-144.7	182.8		
benzene (SRK)	1.91	8.27	0.91	-1.94	13.14	-41.1	50.8		
benzene (PR)	2.04	7.42	0.74	-1.36	10.79	-34.93	43.72		
toluene (SRK)	2.52	10.39	1.01	-2.11	14.07	-45.4	57.1		
toluene (PR)	2.70	9.33	0.83	-1.47	11.41	-38.2	48.9		
methanol	0.68	4.61	0.90	-2.47	3.26	0.0	0.0	0.465	24913
ethanol	1.13	6.40	1.04	-1.46	-0.79	3.8	0.0	0.165	24913
1-butanol	2.07	9.45	1.13	-1.38	8.04	-31.5	37.8	0.065	24913
1-octanol	4.48	17.17	1.63	-6.76	35.8	-81.8	67.7	0.065	24913
ethylene glycol	1.72	6.87	1.10	-3.64	12.16	-37.1	42.5	0.162	24913
1,3-propanediol	2.25	8.27	1.37	-2.50	6.27	-23.1	28.4	0.075	24913
water	0.43	2.39	0.56	-2.54	-2.01	1.5	8.6	0.483	22013

Table A2 – Information on the volume shifts fitted for each compound. When fitted to density the volume shift was always determined at 0.7 T_r.

Compound	equation	volume shift ($dm^3.kmol^{-1}$)		*T* of fitting (K)
		fit density	fit speed of sound	fit speed of sound
water	CPA	11.6	2.9	383
methanol	CPA	18.6	6.7	298
ethanol	CPA	19.1	5.8	293
1-butanol	CPA	17.0	5.2	318
1-octanol	CPA	28.9	9.6	313
ethylene glycol	CPA	20.4	1.5	293
1,3-propanediol	CPA	18.8	11.5	330
n-hexane	SRK	19.4	-38.8	323
n-hexane	PR	0.6	-29.9	323
n-decane	SRK	47.8	-28.0	313
n-decane	PR	16.3	-10.0	313
n-hexadecane	SRK	116.9	3.0	328
benzene	SRK	14.1	-23.9	323
benzene	PR	0.4	-17.9	323
toluene	SRK	18.6	-22.3	323
toluene	PR	2.3	-14.1	323

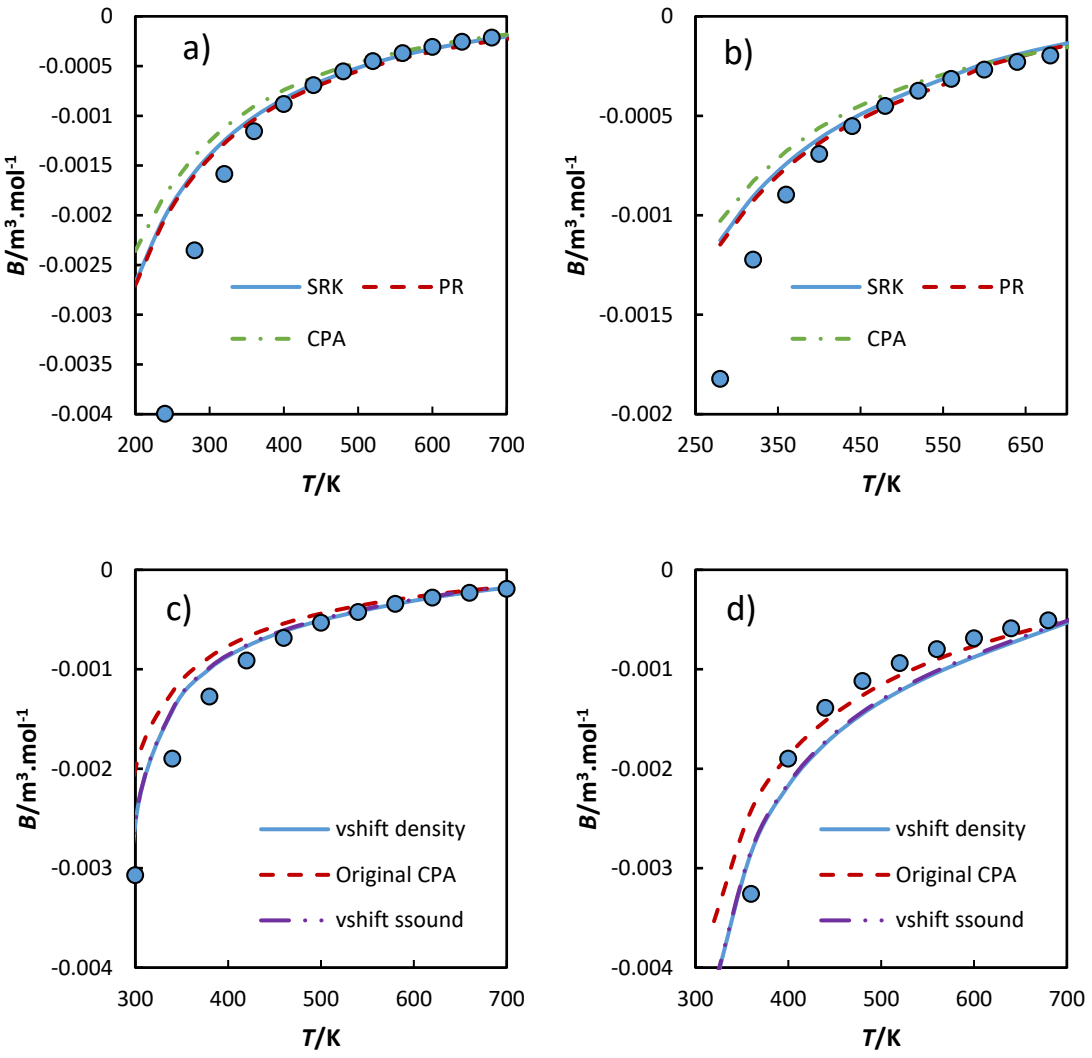

Figure A1 – Second virial coefficient for hexane (a), benzene (b), 1-butanol (c) and 1-octanol (d). CPA parameters are from Oliveira et al. [1] Data taken from the correlations present on Multiflash. [2]

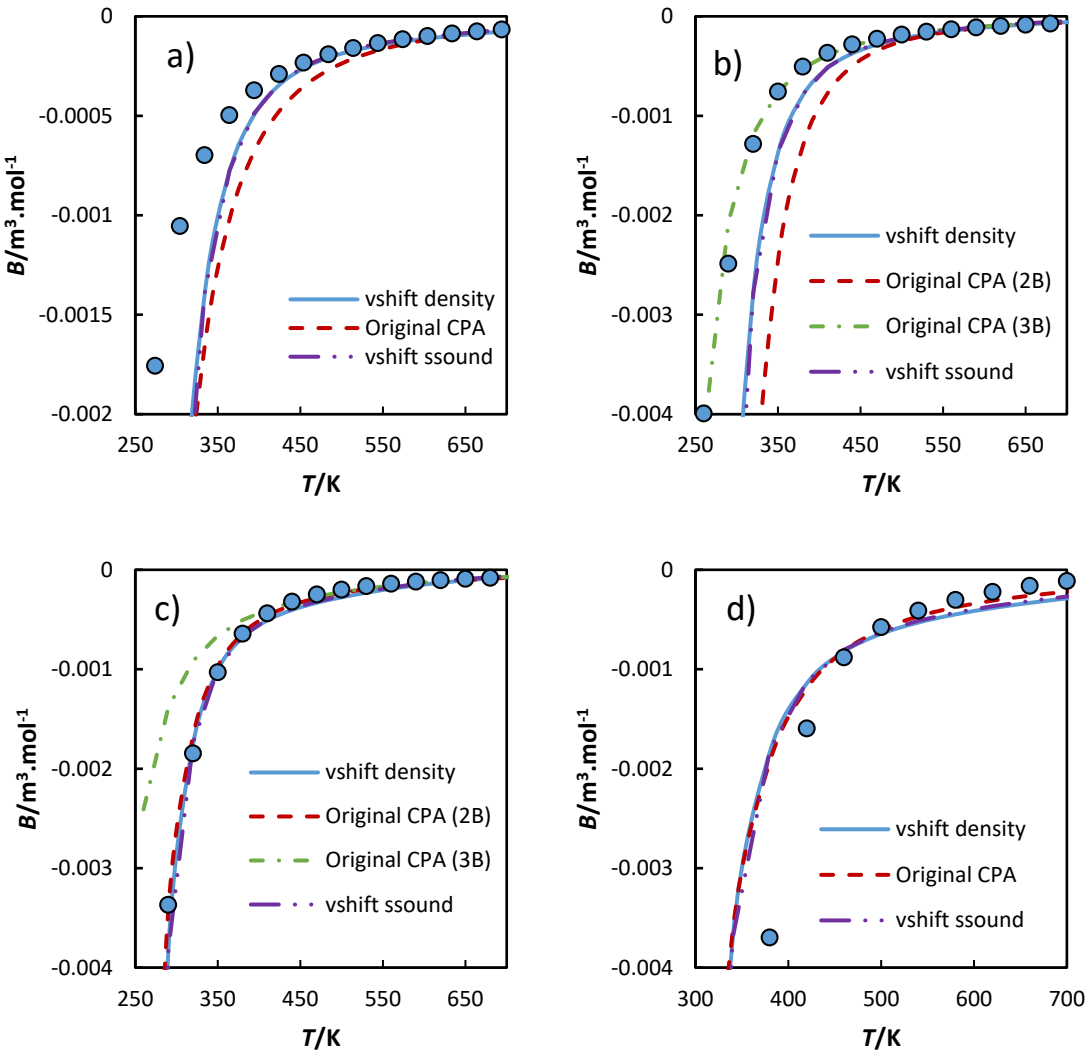

Figure A2 – Second virial coefficient for a) water, b) methanol, c) ethanol and d) ethylene glycol. Original CPA parameters taken from a CPA review. [3] Data taken from the correlations of Multiflash. [2]

References

(1) Oliveira, M. B.; Marrucho, I. M.; Coutinho, J. A. P.; Queimada, A. J. Surface Tensions of Chain Molecules through a Combination of the Gradient Theory with the CPA EoS. *Fluid Phase Equilib.* **2008**, *267* (1), 83–91. https://doi.org/10.1016/j.fluid.2011.01.015.

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(3) Kontogeorgis, G. M.; Michelsen, M. L.; Folas, G. K.; Derawi, S.; Von Solms, N.; Stenby, E. H. Ten Years with the CPA (Cubic-Plus-Association) Equation of State. Part 1. Pure Compounds and Self-Associating Systems. *Ind. Eng. Chem. Res.* **2006**, *45* (14), 4855–4868. https://doi.org/10.1021/ie051305v.