Supporting Information

Measurements and Modelling of Vapour-Liquid Equilibrium for (H_2O + N_2) and (CO_2 + H_2O + N_2) Systems at Temperatures Between (323 and 473) K and Pressures up to 20 MPa

Yolanda Sanchez-Vicente[1,2]* and J P Martin Trusler [1]

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Sensitivity analysis of parameters

A sensitive analysis has been carried out to see the impact of the optimised parameters in the SAFT-γ Mie result. The approach used in this paper is One-At-A-Time (OAT). This approach consists of modifying each optimised model parameter by ±5% of its optimate value and keeping all the other parameters fixed to their original values. This effect is analysed by calculating the absolute and relative average deviation between a particular property's experimental and estimated value. The definition of the average absolute deviation (Δ_{AAD}) is defined

$$\Delta_{AAD} = \frac{\sum(|\chi_{cal} - \chi_{exp}|)}{N} \quad \text{(S1)}$$

And the average absolute relative average deviation (Δ_{AARD}) is defined:

$$\Delta_{AARD} = \frac{1}{N}\sum \frac{(|\chi_{cal} - \chi_{exp}|)}{\chi_{exp}} \quad \text{(S2)}$$

Here, χ_{exp} and χ_{cal} are the thermophysical property obtained experimentally and calculated with SAFT-γ Mie, respectively. N, is the number of data

S1. Pure nitrogen

We have modelled nitrogen as molecular group N_2 with two fused segments, ν_k^* =2 and the attractive exponent is fixed to the London value = 6. The rest of the parameters were obtained by regression of pure nitrogen properties. The optimised parameters used in this sensitivity analysis were S_k, the shape factor, σ_{kk}, size of group k, λ^r_{kk}, the repulsive exponent and ε_{kk}, the Mie potential dispersion energy. Table S1 shows the optimised and modified parameter sets. The effect of each modified parameter is analysed in four calculated properties: vapour pressures, p_{vap}, saturated liquid densities, ρ_{sat}, single-phase densities, ρ, and heat capacity, c_p, of pure nitrogen[1-3]. The Δ_{AARD} between the experimental and calculated data obtained after modifying each mentioned parameter by ±5% of its optimate value are presented in Table S1. The most affected property by the parameter perturbation was p_{vap} with Δ_{AARD} from 13.5 % to 40.0 %. S_k, λ^r_{kk} and ε_{kk} are the most sensitive parameter on this property with Δ_{AARD} 26.5 %, 25.9 % and 40.0 %. The single-phase density was the least affected, with an Δ_{AARD} of less than 3%. This might suggest that the density prediction by SAFT-γ Mie is quite reliable.

Table S1. The optimised and modified group parameters used in the SAFT-γ Mie sensitive analysis for pure nitrogen. S_k, the shape factor and σ_{kk} size of group k, λ^r_{kk} , the repulsive exponent, and ε_{kk} Mie potential dispersion

energy. k_B is Boltzmann constant, k_B=1.380648813·10^{-23} J K^{-1}. Absolute average relative deviations (ΔAARD) between experimental and calculated values obtained with SAFT-γ Mie approach. p_{vap}, ρ_{sat}, ρ, c_p are vapour pressure, saturated-Liquid density, single-phase density and isobaric specific heat capacity, respectively. N denotes the number of points

	S_k	σ_{kk}/ Å	λ^r_{kk}	(ε_{kk}/k_B)/K	*N*	*Range T/K*	p_{vap}	ρ_{sat}	ρ	c_p
							10·Δ_{AARD}			
Optimized	0.7101	3.1779	10.1087	73.64	284	64-693	0.39	0.50	0.80	17.6
Set 1a	**0.7456**	3.1779	10.1087	73.64			20.21	3.39	1.43	19.79
Set 1b	**0.6746**	3.1779	10.1087	73.64			26.49	8.10	1.14	28.45
Set 2a	0.7101	**3.3368**	10.1087	73.64			13.50	13.71	2.84	18.50
Set 2b	0.7101	**3.0190**	10.1087	73.64			16.80	16.51	2.65	31.67
Set 3a	0.7101	3.1779	**10.6141**	73.64			25.90	15.29	1.45	27.11
Set 3b	0.7101	3.1779	**9.6033**	73.64			21.28	5.99	1.73	25.10
Set 4a	0.7101	3.1779	10.1087	**77.32**			26.77	7.52	1.46	27.22
Set 4b	0.7101	3.1779	10.1087	**69.96**			39.99	23.92	1.33	29.99

S2. CO_2+N_2 system

The unlike dispersion energy (ε_{kk}) and the repulsive exponent (λ^r_{kl}) between CO_2 and N_2 groups were the optimised parameters employed in this sensitivity analysis for the CO_2+N_2 system. The optimised and modified parameter sets are shown in Table S2. The bubble and dew point composition of carbon dioxide[4] were used to examine the impact of each modified parameter by ±5% of its optimate value. Table S2 presents the Δ_{AAD} and Δ_{AARD} between the experimental and calculated data obtained after modification. As shown in Table S2, ε_{kk} is the most sensitive parameter on the bubble point composition, with Δ_{AARD} at around 4 %, indicating that the bubble point composition is a good data set for parameter optimisation. The dew point composition deviations were almost unaffected by these small parameter changes.

Table S2. The optimised and modified group parameters used in the SAFT-γ Mie sensitive analysis for the CO_2+N_2 system. Unlike group dispersion interaction energies, ε_{kk}, repulsive exponent, λ^r_{kl} and k_B is Boltzmann constant, k_B=1.380648813·10^{-23} J K^{-1}. Absolute average deviations (Δ_{AAD}) and absolute average relative deviations (Δ_{AARD}) between experimental and calculated values obtained with SAFT-γ Mie approach. The subscript x and y indicate bubble and dew point molar fraction composition of CO_2, respectively. N denotes the number of points

System	group, *k*	Group *l*	(ε_{kk}/k_B)/K	λ^r_{kl}	*N*	Range *T*/K	Δ_{AADx}	Δ_{AADy}	Δ_{AARDx}	Δ_{AARDy}
Optimated	CO_2	N_2	151.9	20.27	68	218-288	0.017	0.023	1.5	2.1
Set 1a			159.5	20.27			0.044	0.023	4.0	2.1
Set 1b			144.3	20.27			0.043	0.028	3.9	2.6
Set 2a			151.9	21.28			0.022	0.025	2.0	2.3
Set 2a			151.9	19.26			0.021	0.023	1.9	2.1

S3. H_2O+N_2 system

Only unlike dispersion energy (ε_{kk}) between H_2O and N_2 groups was employed in this sensitivity analysis for the H_2O+N_2 system. The impact of modifying this parameter by ±5% of its optimate value was measured in the deviations of dew and bubble point composition of nitrogen obtained in this work and presented in Table S3. As seen in the table, increasing the value of this parameter by 5% has little effect on the deviation of the bubble and dew point compositions. Whereas reducing the energy by 5% has a considerable influence on both compositions. This might indicate that we need more data to determine the effect of these parameters on the mole fraction composition.

The sensitivity analysis results should be taken with caution because the apparent sensitivity of the model for a given parameter depends on the selected property, the number of data, and the optimised value. It should be noted that the OAT model is the simplest approach for sensitivity analysis. It only addresses sensitivity to the local point chosen, not the complete parameter distribution.

Table S3. The optimised and modified group parameters used in the SAFT-γ Mie sensitive analysis for the CO2+N2 system. Unlike group dispersion interaction energies, ε_{kk} and k_B is Boltzmann constant, kB=1.380648813·10−23 J K^{-1}. Absolute average deviations (Δ_{AAD}) and absolute average relative deviations (Δ_{AARD}) between experimental and calculated values obtained with SAFT-γ Mie approach. The subscript x and y indicate bubble and dew point molar fraction composition of N_2, respectively. N denotes the number of points

System	group, *k*	Group *l*	(ε_{kk}/k_B)/K	*N*	Range *T*/K	Δ_{AADy}	Δ_{AADy}	Δ_{AARDy}	Δ_{AARDy}
Optimated	H_2O	N_2	126.59	50	323-423	0.00014	0.008	25	1.1
Set 1a			132.92			0.00020	0.010	21	1.4
Set 1b			120.26			0.00028	0.067	70	9.9

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