

Modelling of phase equilibria of glycol ethers mixtures using an association model

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ABSTRACT

Vapor–liquid and liquid–liquid equilibria of glycol ethers (surfactant) mixtures with hydrocarbons, polar compounds and water are calculated using an association model, the Cubic-Plus-Association Equation of State. Parameters are estimated for several non-ionic surfactants of the polyoxyethylene type but mixture calculations are mostly presented for three compounds for which many data are available (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol). The way pure compound vapor pressures and liquid densities are estimated, and the way parameter trends against the van der Waals volume, Kamlet–Taft parameters and, perhaps most importantly, mixture liquid–liquid equilibria data with alkanes are used for choosing optimum parameter sets is illustrated. Vapor–liquid, liquid–liquid equilibria and second virial coefficient data are used for model validation, including aqueous and other cross-associating mixtures. The influence on the results of the association schemes, type of data available, combining rules for cross-associating mixtures and interaction parameters are discussed also in connection to other cross-associating mixtures, previously studied with the model. Finally, the capabilities and limitations of the Cubic-Plus-Association Equation of State in representing this type of multi-functional chemicals, glycol ethers, are discussed.

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1. Introduction

Oil industry uses a large number of associating chemicals (alcohols, glycols, amines, alkaloamines, glycol ethers, ionic surfactants, etc.) which serve various purposes, e.g., as gas-hydrate inhibitors, corrosion, scale or wax inhibitors, antifoamers, flocculants, solvents, emulsion breakers, etc. The distribution of these chemicals in oil and water needs to be known not only to satisfy specifications of the oil and ensure production, but also to satisfy environmental regulations. There are two ways for obtaining this distribution: via direct (experimental) measurements of oil–water partition coefficient of the chemicals or indirectly, via estimation of the octanol–water partition coefficient of the chemicals (provided that the latter is related satisfactorily to the oil–water one). Octanol–water

coefficients together with other related information (bioconcentration, biodegradation, toxicity) must be reported to the authorities.

This work focuses on the investigation of a thermodynamic model, the Cubic-Plus-Association (CPA) equation of state (EoS), in calculating phase equilibria for a specific type of non-ionic surfactants (glycol ethers) towards (in the future) predicting distribution coefficients in octanol–water and oil–water mixtures. Having a thermodynamic model is quite advantageous for this kind of compounds, since due to surface adsorption, K_{OW} (octanol–water partition coefficient) measurements are difficult for surfactants. While performing K_{OW} measurements, the surfactant molecules accumulate at the octanol–water interface, which results in lower surfactant concentrations in the bulk solvent [1,2]. At the same time, the surfactants may also form emulsions and enhance the mutual solubility of octanol and water by strong interaction with octanol even below their critical micelle concentration [2].

The unusual properties of aqueous surfactant solutions can be ascribed to the presence of the hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole–dipole or ion–dipole interactions.

Abbreviations: AAD, absolute average deviation; CPA, Cubic-Plus-Association; DIPPR, Design Institute for Physical Property (database); ECR, Elliott combining rule; EG, ethylene-glycol; EoS, equation of state; LLE, liquid–liquid-equilibrium; SAFT, statistical association fluid theory; SLE, solid–liquid-equilibrium; SRK, Soave–Redlich–Kwong equation of state; VLE, vapor–liquid-equilibrium.

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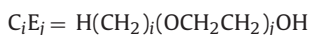
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Table 1
The DIPPR deviations based on DIADDEM software [15]

Surfactant	ρ_L deviation (kmol m ⁻³)		P_S deviation (Pa)		Number of data points		T_r range	
	Av.	Max.	Av.	Max.	ρ_L	P_S	ρ_L	P_S
C ₁ E ₁	0.1	0.3	1.4	8.8	50	139	0.51–0.64	0.34–1.00
C ₂ E ₁	0.1	0.5	2.5	21.8	50	88	0.51–0.63	0.32–1.00
C ₄ E ₁	0.1	0.1	1.7	12.0	65	93	0.48–0.59	0.34–1.00
C ₄ E ₂	0.1	0.3	5.7	16.5	8	40	0.42–0.43	0.43–0.73
C ₄ E ₃	0.1	0.1	3.8	31.0	8	30	0.43–0.54	0.33–0.86

The experimental errors in terms of vapor pressures (P_S) and liquid densities (ρ_L), the temperature range and the number of data points available are presented. Av. and Max. indicate the average and maximum deviations.

Many types of surfactants are of interest to the oil and chemical industries, but in the present work we focus on one type of non-ionic surfactants, the alkyl polyoxyethylene ethers. These multi-functional compounds can be represented by the general formula C_iE_j, where *E* represents the oxyethylene group, the subscript *i* is the number of alkyl carbons in the hydrophobic-group and *j* is the number of hydrophilic (oxyethylene) groups:



The glycol ethers to be studied in this work are: 2-methoxyethanol–C₁E₁ (C₃H₈O₂), 2-ethoxyethanol–C₂E₁ (C₄H₁₀O₂), 2-butoxyethanol–C₄E₁ (C₆H₁₄O₂), 2-(2-butoxyethoxy)ethanol–C₄E₂(C₈H₁₈O₃), and 2-(2-(2-butoxyethoxy)ethoxy)ethanol–C₄E₃ (C₁₀H₂₂O₄) also known as triethylene glycol butyl ether. All contain one OH group, those with E₁ contain one additional O atom, those with E₂ two O atoms and C₄E₃ contains three additional O atoms.

Generally, the applications of glycol ethers in industry are quite diverse and of great practical importance. Glycol ethers may be applied in the production and processing of foods, agrochemicals, pharmaceuticals, personal care and laundry products, petroleum, mineral ores, fuel additives and lubricants, paints, coatings and adhesives and photographic films. They can also be found throughout a wide spectrum of biological systems and medical applications, soil remediation techniques, and other environmental and safety applications. Namely, some examples of surfactants application in the petroleum industry [3] include gas–liquid systems (producing oil well and well-head foams, oil flotation process froth, distillation and fractionation tower foams, fuel oil and jet fuel tank (truck) foams, foam drilling fluid, foam fracturing fluid, foam acidizing fluid, blocking and diverting foams, gas-mobility control foams), liquid–liquid systems (emulsion drilling fluids, enhanced oil recovery in situ emulsions, oil sand flotation process slurry, oil sand flotation process froths, well-head emulsions, heavy oil pipeline emulsion, fuel oil emulsions, asphalt emulsions, oil spill emulsions, tanker bilge emulsions) and solid–liquid systems (reservoir wettability modifiers, reservoir fines stabilizers, tank/vessel sludge dispersants, drilling mud dispersants).

As previously referred, in this work, the CPA EoS, which is a statistical association fluid theory (SAFT) variant, will be applied. A few investigations related with the applicability of SAFT type EoS to surfactant mixtures [4–6] can be found in the literature. The CPA EoS has been presented in the literature including in recent reviews [7–14]. For this reason the model equations are only summarized in Appendix A. For cross-associating mixtures, a choice must be made between several mixing rules. They are labelled ECR and CR-1 and their meaning is recalled in Appendix A.

Next, we will describe the procedure to obtain the CPA parameters used in this work and briefly discuss the quality (and its importance) of the input data used in the regression. In Section 3 we will present and discuss the performance of CPA when representing both VLE and LLE and show a new method to improve the LLE prediction keeping the VLE prediction quite good. Afterwards,

we will present some second virial coefficients and octanol–water partition coefficients predictions for the glycol ethers under study. Finally, the capabilities of the CPA in predicting this type of phase equilibria calculations will be analyzed.

2. Pure compound parameters

Important input data for the development of thermodynamic SAFT-type models are vapor pressures and liquid densities. It may be tempting to use the correlations proposed by DIPPR as pseudo-experimental data. Yet, for complex multi-functional compounds, the validity range of the correlations as provided by DIPPR [15] may be much larger compared to the actual data used in the development of these correlations. This is a limitation and care should be exercised in use of these correlations as pseudo-experimental data for parameter regression.

Table 1 shows the range of DIPPR correlations used in this work and also the deviations (average and maximum) when compared to the available experimental data, while Figs. 1 and 2 illustrate a comparison of DIPPR correlations for the density and vapor pressure against the actual experimental data [15] for the glycol ethers under study in the present work.

From Figs. 1 and 2, we can observe that it is particularly density data which are lacking and some times disagreement among different sources is also observed. This is the case for C₄E₂ and C₄E₃, where at constant temperature the liquid density data can vary around 30 mol m⁻³ when different data sources are compared for the same compound. Briefly, the reduced temperature range over which density data are available is narrow and the deviations presented in Table 4 (pure compound CPA parameters) are higher when a wide range of temperatures is used.

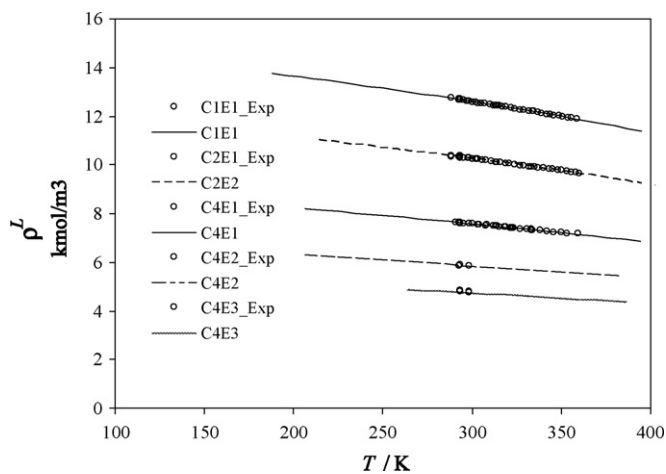


Fig. 1. Evaluation of DIPPR correlations [17] against liquid density (ρ_L) data for the selected glycol ethers.

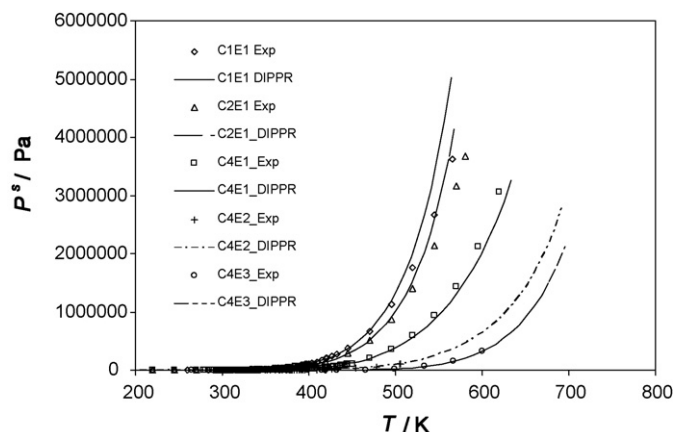


Fig. 2. Evaluation of DIPPR correlations [17] for vapor pressure (P_s) data for the selected surfactants.

Table 2
Kamlet–Taft parameters for some surfactants

	α	β	π	Reference
C ₁ E ₁	0.770	0.720	0.720	[17]
C ₄ E ₁	0.586	0.682	0.687	[18]
C ₄ E ₂	0.278	0.227	1.089	[18]

Other useful pure compound data for parameter estimation, especially for the association parameters, are the monomer fraction and enthalpies and entropies of association, often obtained from spectroscopic measurements. Some few monomer fraction data are available [16] where also the effect of intramolecular association is studied for two glycol ethers. Also, a useful measure of association is offered by the so-called Kamlet–Taft parameters, which provide a measure of the acidity/basicity of compounds. The three Kamlet–Taft solvent scale parameters available in the literature are the solvent hydrogen-bond donor ability, α , the solvent hydrogen-bond acceptor ability β , and the solvent dipolarity/polarizability π . Table 2 presents the data available for three glycol ethers [17,18]. This Kamlet–Taft values numerically quantify solvent–solute interactions that are representative in all types of solution equilibrium. The values from Table 2 can indicate that the association characteristics of these glycol ethers should be quite different, but it is not possible to include directly this information in the CPA regression

procedure. However, in agreement with this expectation, also both association parameters (the association energy parameter ε , and the association volume parameter, β) obtained for the five glycol ethers are considerable different (see Table 4).

Tables 3 and 4 present the model parameters for the inert and associating compounds, respectively, considered in this work. The absolute average deviations (AAD) are calculated as:

$$\Delta P_s(\%) = \frac{100}{n_{\text{data}}} \sum_{i=1}^{n_{\text{data}}} \left| \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right| \quad (1)$$

$$\Delta \rho_L(\%) = \frac{100}{n_{\text{data}}} \sum_{i=1}^{n_{\text{data}}} \left| \frac{V_i^{\text{exp}} - V_i^{\text{calc}}}{V_i^{\text{exp}}} \right| \quad (2)$$

The parameters are optimized based on vapor pressures and liquid density data [13], assuming either the 2B or 3B association schemes (following the terminology from Huang and Radosz [21]), in agreement to previous studies for alcohols. Both schemes correlate equally well vapor pressures and liquid densities for glycol ethers, and the parameters will be further tested to mixture data.

It was observed that if we increase the upper regression limit to 0.95, the percentage deviation between experimental and calculated liquid densities and vapor pressures increases significantly, especially for the liquid density.

The investigation we carry out here is based on a so-called first-step approach, i.e., an evaluation of the model performance under certain simplifying assumptions:

- no special treatment of polarity, only the association term of CPA or SAFT is used.
- existing association schemes, like 2B and 3B will be used, i.e., only considering the OH of glycol ethers.
- no explicit treatment of the oxygen or number of oxygen atoms is considered.
- no intramolecular association will be considered.

3. Results and discussion

3.1. Vapor–liquid-equilibria

Figs. 3–6 present some typical results for mixtures of four glycol ethers with inert and polar or associating compounds, while Tables 5 and 6 present an overview of the results for (mostly) cross-associating isothermal or isobaric systems against the available

Table 3
CPA parameters for the inert compounds considered in this work, obtained by regressing vapor pressure and saturated liquid volume data in the T_r (reduced temperature) range of 0.55–0.9

Component	a_0 (bar L ² mol ⁻²)	b (L mol ⁻¹)	c_1	T_C (K)	ΔP_s (%)	$\Delta \rho_L$ (%)	Ref.
Toluene	23.375	0.09214	0.8037	591.80	0.2	0.6	[8]
<i>n</i> -Octane	34.875	0.14244	0.9942	568.70	0.4	0.6	[8]
Octene	33.630	0.13780	0.9700	566.60	1.2	1.0	[9]
Benzene	17.876	0.07499	0.7576	562.16	0.9	1.0	[8]
Methyl acetate	14.593	0.06625	0.8719	506.55	–	–	[19]
Ethyl acetate	18.880	0.08338	0.9427	523.30	–	–	[19]
<i>n</i> -Hexane	23.681	0.10789	0.8313	507.60	0.5	0.5	[8]
1-Hexene	21.983	0.10200	0.8430	617.05	0.1	0.7	[9]
Ethylbenzene	28.860	0.10872	0.8539	617.20	0.2	0.4	[8]
<i>n</i> -Dodecane	62.403	0.21624	1.1953	658.00	1.1	1.0	[9]
<i>n</i> -Heptane	29.178	0.12535	0.9137	540.20	0.3	0.5	[8]
<i>n</i> -Hexadecane	94.914	0.29610	1.3728	723.00	0.4	1.8	[10]
2-Methylpentane	22.8205	0.107757	0.83732	497.50	0.1	0.8	This work
2-Methylhexane	28.327	0.124720	0.89910	530.37	0.4	0.7	This work
2-Methylheptane	34.1842	0.141885	0.96008	559.64	0.1	0.5	This work
2,4-Dimethylhexane	33.3033	0.141199	0.92763	553.50	0.2	0.6	This work
2,2,4-Trimethylpentane	32.2332	0.139164	0.86803	543.96	0.2	0.9	This work
Ethylcyclohexane	32.3264	0.124584	0.82473	609.15	0.8	0.7	This work

Table 4
CPA parameters for the associating compounds considered in this work, obtained by regressing vapor pressure and saturated liquid volume data in the T_r range of 0.55–0.90

Component	a_0 (bar L ² mol ⁻²)	b (L mol ⁻¹)	c_1	$\varepsilon^{A_i B_j}$ (bar L mol ⁻¹)	$\beta^{A_i B_j}$	T_c (K)	ΔP_s (%)	$\Delta \rho_L$ (%)	Reference
EG	10.819	0.05140	0.674	197.52	0.0141	750.00	0.9	1.6	[12]
Water	1.228	0.01452	0.674	166.55	0.0692	647.29	0.8	0.5	[11]
Methanol	4.053	0.03098	0.431	245.91	0.0161	512.64	0.6	0.5	[11]
Ethanol	8.672	0.04908	0.737	215.32	0.0080	513.92	1.3	0.3	[8]
Propanol	11.910	0.06413	0.917	210.01	0.0081	536.78	0.4	0.5	[8]
1-Butanol	15.695	0.07970	0.978	210.01	0.0082	563.05	0.9	1.0	[8]
1-Octanol	41.582	0.14845	1.1486	267.59	0.00014	652.50	0.8	0.5	[20]
C ₁ E ₁ (2B)	8.013	0.06459	1.051	228.23	0.0669	564.00	1.8	0.3	This work
C ₁ E ₁ (3B)	7.005	0.06491	1.425	200.49	0.0499	564.00	1.7	0.3	This work
C ₂ E ₁ (2B)	9.770	0.07785	0.780	276.38	0.0228	569.00	1.5	0.3	This work
C ₂ E ₁ (3B)	8.947	0.07986	1.314	224.90	0.0261	569.00	1.3	0.3	This work
C ₄ E ₁ (2B)	17.933	0.11531	1.438	186.66	0.1260	600.0	0.6	0.2	This work
C ₄ E ₁ (3B)	15.679	0.11526	1.748	162.40	0.1020	600.0	1.3	0.2	This work
C ₄ E ₂ (2B)	20.381	0.15532	2.092	185.70	0.3210	692.30	4.1	0.5	This work
C ₄ E ₂ (3B)	17.014	0.15319	2.290	198.06	0.1116	692.30	4.2	0.4	This work

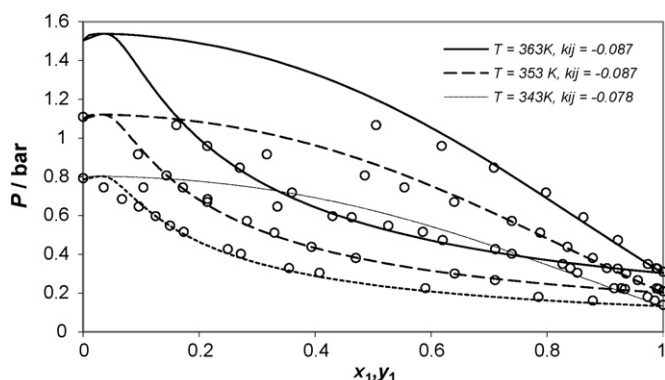


Fig. 3. Comparison between experimental VLE data [22] (points) and CPA correlation (lines) for the system C₁E₁ (2B) + ethyl acetate with the optimal k_{ij} at different temperatures. Similar results are obtained using the 3B scheme for C₁E₁.

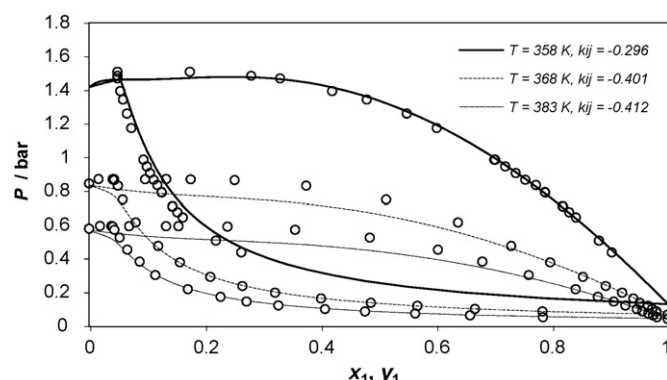


Fig. 5. Comparison between experimental VLE data [25,26] (points) and CPA prediction/correlation (lines) for the system C₄E₁ (2B) + water using ECR.

experimental data. In the case of cross-associating systems only the CR-1 and ECR combining rules are tested. Results with other combining rules (CR-2, CR-4) will not be shown, as results from previous studies showed that they systematically fail to correlate cross-associating systems [12,13,19]. Moreover, the CR-3 combining rule usually provides similar results to CR-1 [19]. The bold lines in Tables 5, 6 and 8 mean the combination between association schemes, combining rules and binary interaction parameters that better represent each system.

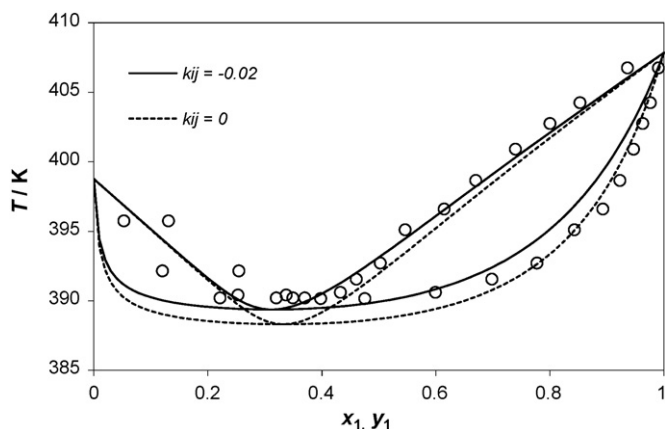


Fig. 4. Comparison between experimental VLE data [23,24] (points) and CPA prediction/correlation (line) for the azeotropic system C₂E₁ (2B or 3B—the lines coincide) + n-octane. $P = 1.01$ bar.

In most cases results are presented using either $k_{ij} = 0$ (prediction) or using a single-fitted interaction parameter, which is the correction to the geometric mean rule of the energy parameter, in the SRK part of the model.

The basic conclusions are summarized hereafter:

1. Excellent VLE correlation is obtained for all mixtures (except those with water) using a single k_{ij} value per binary and in many cases pure predictions ($k_{ij} = 0$) yield satisfactory results,
2. Concerning VLE, there is little difference in using the 2B or 3B scheme for the glycol ethers (except for aqueous mixtures, see discussion later),

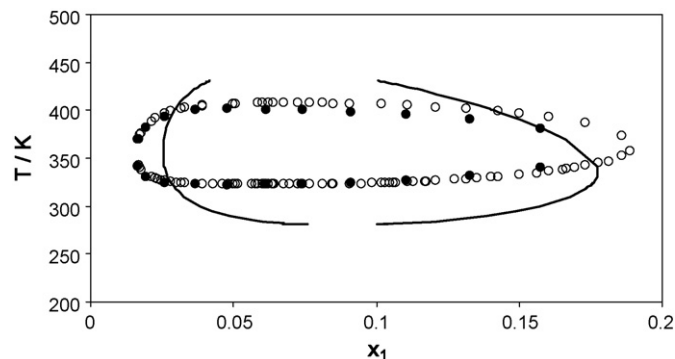


Fig. 6. CPA prediction of the LLE for the system 2-butoxyethanol (3B) + water (4C), using CR-1 rule and $k_{ij} = -0.192$. 3B is the only choice in this case. Closed circles are experimental data from [27] and open circles are data from [28,29].

Table 5

Correlation performance of the CPA EoS for surfactant mixtures VLE, especially cross-associating mixtures

System	Reference	T (K)	2B				3B			
			k_{12}	CR	$\Delta P\%$	Δy^*100	k_{12}	CR	$\Delta P\%$	Δy^*100
C_1E_1 + water	[25,30]	363.15	0.000	CR-1	25.9	8.4	0.000	CR-1	12.9	7.2
			−0.217	CR-1	6.4	1.9	0.104	CR-1	12.0	6.3
			0.000	ECR	48	13.7	0.000	ECR	8.0	4.2
			−0.343	ECR	1.8	0.6	0.024	ECR	9.2	4.6
		343.15	0.000	CR-1	31.1	9.9	0.000	CR-1	13.3	8.0
			−0.232	CR-1	3.3	2.2	0.085	CR-1	13.1	7.5
			0.000	ECR	56.3	15.4	0.000	ECR	9.3	4.9
			−0.350	ECR	1.9	0.7	−0.030	ECR	8.7	5.0
C_1E_1 + methanol	[39]	298.15	0.000	CR-1	1.1	1.0	0.000	CR-1	27.4	5.8
			0.003	CR-1	1.0	0.9	0.113	CR-1	3.4	0.8
			0.000	ECR	3.7	0.6	0.000	ECR	24.1	5.0
			−0.013	ECR	1.2	0.9	0.096	ECR	3.3	0.8
C_1E_1 + propanol	[32]	343.15	0.000	CR-1	3.5	1.7	0.000	CR-1	16.5	4.6
			0.014	CR-1	1.2	1.9	0.112	CR-1	1.6	1.7
			0.000	ECR	3.5	1.7	0.000	ECR	16.5	4.6
			0.014	ECR	1.2	1.9	0.112	ECR	1.6	1.7
C_1E_1 + ethyl acetate	[33]	343.15	0.000	–	25.0	6.2	0.000	–	29.0	7.0
			−0.078	–	7.7	1.8	−0.089	–	8.4	1.9
		353.15	0.000	–	27.9	6.8	0.000	–	32.2	7.8
			−0.087	–	4.4	1.7	−0.099	–	5.1	1.9
		363.15	0.000	–	26.2	7.2	0.000	–	30.8	8.6
			−0.087	–	3.9	1.5	−0.100	–	4.4	8.7
C_2E_1 + water	[25]	363.15	0.000	CR-1	29.8	5.2	0.000	CR-1	20.0	9.9
			−0.229	CR-1	5.7	3.1	0.139	CR-1	17.9	8.6
			0.000	ECR	64.6	10.5	0.000	ECR	11.5	5.7
			−0.395	ECR	2.2	1.6	−0.026	ECR	11.1	5.6
		343.15	0.000	CR-1	37.9	6.7	0.000	CR-1	19.2	11.2
			−0.257	CR-1	6.6	3.7	0.096	CR-1	21.1	6.9
			0.000	ECR	76.7	13.0	0.000	ECR	14.6	6.8
			−0.407	ECR	2.4	1.6	−0.042	ECR	13.0	7.1
C_2E_1 + methanol	[31]	298.15	0.000	CR-1	10.1	1.13	0.000	CR-1	25.6	4.2
			−0.038	CR-1	4.4	1.8	0.112	CR-1	6.3	1.4
			0.000	ECR	16.3	1.2	0.000	ECR	20.8	3.3
			−0.066	ECR	5.6	1.7	0.083	ECR	6.5	1.3
C_2E_1 + toluene	[34]	330.15	0.000	–	28.8	3.9	0.000	–	26.8	3.8
			−0.089	–	4.3	1.7	−0.080	–	4.6	1.8
C_4E_1 + water	[25,26]	383.15	0.000	CR-1	16.4	2.7	0.000	CR-1	42.5	12.7
			−0.027	CR-1	16.0	2.0	0.302	CR-1	32.5	5.7
			0.000	ECR	68.0	3.3	0.000	ECR	15.6	2.9
			−0.296	ECR	1.2	1.3	−0.019	ECR	15.3	2.3
		368.15	0.000	CR-1	21.3	5.5	0.000	CR-1	24.5	10.9
			−0.123	CR-1	10.8	3.6	−0.065	CR-1	24.9	10.8
			0.000	ECR	–	–	0.000	ECR	13.0	3.8
			−0.401	ECR	7.2	1.9	−0.069	ECR	10.2	3.4
		358.15	0.000	CR-1	22.2	4.8	0.000	CR-1	26.3	11.5
			−0.128	CR-1	11.2	3.5	−0.066	CR-1	26.9	10.8
			0.000	ECR	–	–	0.000	ECR	13.5	3.4
			−0.412	ECR	8.9	2.0	−0.068	ECR	11.0	3.3

The CPA parameters are taken from Table 4. $\Delta P(\%)$ is defined as the average absolute percent error in bubble-point pressure; Δy is defined as the average absolute deviation in vapor phase mole fraction.

- Very good results are obtained for mixtures of glycol ethers with polar or associating compounds such as alcohols—there is essentially no difference whether the ECR or CR1 combining rules are used,
- For mixtures with water, a large negative k_{ij} is required for describing the phase behaviour (indicating that the degree of solvation is underestimated) and in this case the 2B scheme for glycol ethers performs better than the 3B (with a bit higher k_{ij} than with the 3B scheme). Moreover, ECR performs better than CR1 in most cases. High negative k_{ij} values were also observed for other cross-associating mixtures with water studied previously, e.g., glycols and amines [15–17].

3.2. Liquid–liquid-equilibria

After correctly predicting VLE, we will test the parameters from Tables 3 and 4 to LLE systems. However, at this step, two cases where problems have been observed are the LLE of butoxyethanol (C_4E_1)–water and the LLE of glycol ether–alkane mixtures. These are hereafter discussed.

- The correlation of the closed loop LLE of butoxyethanol (C_4E_1)–water is particularly difficult to accurately represent, as shown in Fig. 6. These difficulties were also discussed in the literature [4]. A qualitative correlation has been possible only when the 3B scheme was used for the glycol ether and at a cost of a

Table 6
Correlation performance of the CPA EoS for surfactant isobaric mixtures VLE

System	P (bar)	Reference	2B				3B			
			k_{12}	CR	$\Delta T\%$	Δy^*100	k_{12}	CR	$\Delta T\%$	Δy^*100
C ₁ E ₁ + benzene	1.01	[35]	0	–	0.7	2.1	0	–	1.0	3.1
			–0.05	–	0.2	1.4	–0.07	–	0.3	1.7
C ₁ E ₁ + ethanol	0.99	[36]	0	CR1	0.3	2.5	0	CR1	1.1	4.8
				CR1			0.1	CR1	0.3	2.5
			0	ECR	0.3	2.5	0	ECR	1.2	5.9
				ECR			0.1	ECR	0.2	2.1
C ₂ E ₁ + ethanol	1.01	[37,38]	0	CR1	0.6	1.7	0	CR1	1.0	4.4
			–0.05	CR1	0.2	2.1	0.1	CR1	0.3	1.7
			0	ECR	0.7	1.8	0	ECR	0.9	4.2
			–0.05	ECR	0.2	1.9	0.1	ECR	0.4	1.6
				ECR				ECR		
C ₂ E ₁ + hexene	1.01	[39]	0	–	0.2	1.7	0	–	0.2	1.7
C ₂ E ₁ + octane	1.01	[23,24]	0	–	0.4	4.7	0	–	0.4	4.7
			–0.02	–	0.3	2.8	–0.02	–	0.3	2.8
C ₄ E ₁ + octane	0.53	[40]	0	–	0.5	1.9	0	–	0.4	6.8
C ₄ E ₂ + EG	0.03	[41]	0	CR1	1.6	9.1	0	CR1	0.7	8.9
			–0.1	CR1	0.2	3.8	0.01	CR1	0.6	8.5
			–0.13	ECR	0.05	4.1	0.01	ECR	0.6	7.5
C ₄ E ₂ + EG	0.13	[42]	0	–	0.4	7.3	0	–	0.7	7.0
			–0.02	–	0.3	8.4	–0.05	–	0.3	9.4

The CPA parameters are taken from Tables 3 and 4.

large interaction parameter. The results are particularly sensitive to k_{ij} and the combining rule for this mixture. This performance is quite similar to that of the SAFT-HS (Statistical Association Fluid Theory) reported in [4]. It is also interesting to note that the cross association energy parameter in SAFT-HS is 1803 K, closer to that of CPA-3B (=1970 K) than to that of CPA-2B (=2111 K).

- ii. LLE data are available for several glycol ether–alkane mixtures, but the correlation is generally not very satisfactory, in the sense that both solubilities cannot be correlated with equal accuracy using the same k_{ij} value. Still, these calculations have illustrated that the 2B scheme for glycol ethers performs better than the 3B one.

In previous investigations with CPA, improved parameters of self-associating compounds (alcohols, glycols, etc.) are based both on pure compound properties (vapor pressures and liquid densities) and LLE data with alkanes. Here a different approach is used, based entirely on pure compound data. This approach is explained in the next section.

3.3. Use of CPA parameter trends to improve LLE

It has been recently shown [14] that clear trends exist between the a_0 and the b pure compound parameters of CPA against the van der Waals volume (V_w), especially for the co-volume parameter. Data is compiled in Fig. 7 and applying a linear regression

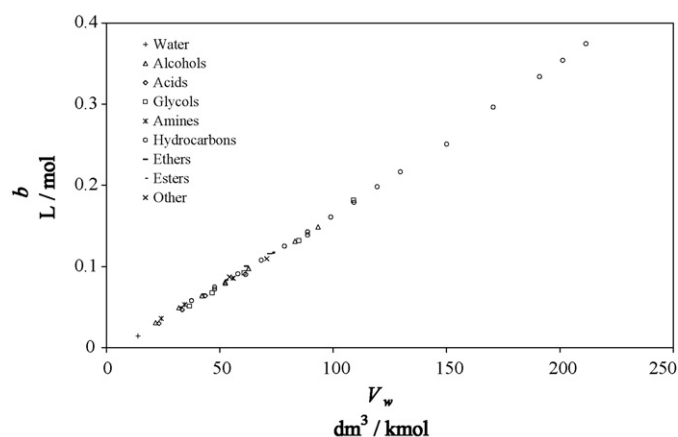


Fig. 7. The co-volume parameter (b) of CPA [14] against the van der Waals volume (V_w) [43] for a variety of compounds.

we can write:

$$b \text{ (L mol}^{-1}\text{)} = 0.0018 V_w \text{ (dm}^3 \text{ kmol}^{-1}\text{)} - 0.0132 \quad (3)$$

The correlation coefficient of this regression is: $r^2 = 0.998$.

Since V_w experimental data are available in the literature for the compounds under study [43], we can obtain the co-volume parameter from Eq. (3) for each one of the glycol ethers. Results

Table 7
New CPA parameters obtained for the surfactants studied, with the $b - V_w$ parameter correlation, see Fig. 7

Component	a_0 (bar L ² mol ^{–2})	b (L mol ^{–1})	c_1	$\varepsilon^{A_i B_j}$ (bar L mol ^{–1})	$\beta^{A_i B_j}$	T_C (K)	ΔP_S (%)	$\Delta \rho_L$ (%)
C ₁ E ₁ (2B)	10.0780	0.0693	1.4025	153.043	0.2154	564.0	2.3	0.8
C ₁ E ₁ (3B)	9.21579	0.0693	1.4637	152.657	0.0915	564.0	2.0	1.2
C ₂ E ₁ (2B)	14.5994	0.0878	1.3675	146.061	0.1453	569.0	2.8	1.3
C ₂ E ₁ (3B)	13.6843	0.0878	1.3257	155.673	0.0540	569.0	2.3	1.7
C ₄ E ₁ (2B)*	32.1728	0.1246	1.2431	19.1517	0.7329	600.0	1.1	1.6
C ₄ E ₁ (3B)*	32.0230	0.1246	1.2451	15.3105	0.4735	600.0	1.1	1.6

V_w data were taken from [43]. The % AAD are defined as in Table 3.

The CPA parameters for the associating compounds marked with * were obtained by regressing vapor pressure and saturated liquid volume data in the T_r range of 0.55–0.88. For the remaining surfactants the T_r range 0.55–0.90 was used.

Table 8

Correlation performance of the CPA EoS for surfactant mixtures VLE using the new set of CPA parameters (from Tables 3 and 7)

System	T (K)	Ref	2B				3B			
			k_{12}	CR	$\Delta P\%$	Δy^*100	k_{12}	CR	$\Delta P\%$	Δy^*100
C ₂ E ₁ + methanol	298.15	[31]	0	CR1	4.3	0.3	0	CR1	17.0	1.8
	313.15		0	CR1	2.0	1.1	0	CR1	4.5	2.8
	323.15		0	CR1	1.2	2.0	0	CR1	14.2	3.8
	333.15		0	CR1	1.0	2.3	0	CR1	9.7	4.1
C ₁ E ₁ + Methanol	298.15	[39]	0	CR1	5.5	0.3	0	CR1	21.2	3.5
			0	ECR	1.4	1.1	0	ECR	16.7	2.5
C ₁ E ₁ + water	343.15	[25,30]	0	CR1	27.2	9.9	0	CR1	8.7	5.4
			0	ECR	52.9	15.5	0	ECR	4.7	4.8
			−0.18	CR1	3.7	2.2	−0.02	CR1	3.0	5.6
			−0.29	ECR	2.3	1.5	−0.10	ECR	3.9	2.2
	343.15		0	CR1	22.8	0.6	0	CR1	8.4	4.9
			0	ECR	46.9	14.0	0	ECR	10.4	4.4
			−0.18	CR1	3.1	2.1	−0.04	CR1	3.4	2.3
			−0.29	ECR	2.2	1.3	−0.10	ECR	4.4	3.4
C ₁ E ₁ + propanol	343.15	[32]	0	CR1	6.6	1.9	0	CR1	13.5	3.5
			0	ECR	6.6	1.9	0	ECR	13.5	3.5
C ₁ E ₁ + ethyl acetate	343.15	[33]	0	–	16.1	4.0	0	–	22.1	5.6
			−0.045	–	6.9	1.6	−0.06	–	7.2	1.7
	353.15		0	–	18.4	5.3	0	–	25.3	6.1
			−0.053	–	3.8	1.2	−0.07	–	3.8	1.7
	363.15		0	–	17.1	5.6	0	–	24.3	6.7
			−0.052	–	3.4	1.0	−0.07	–	3.6	1.5

are included in bold in Table 7. So, the approach used in order to improve the LLE calculations for the glycol ether–alkane mixtures consisted of the estimation of new CPA pure compound parameters by fixing the co-volume b to the value obtained from Eq. (3) and then fitting the remaining four parameters to vapor pressure and liquid density data. These new CPA parameters are presented in Table 7.

The most important difference for the small glycol ethers, C₁E₁ and C₂E₁, between the new parameters and the ones presented in Table 4 is a slight decrease in the energy parameter. The values obtained for the associating parameters of C₄E₁ are quite different from those of Table 4, as the association energy parameter is much lower and the association volume parameter is quite higher than the parameters obtained so far with CPA.

VLE tests with this new set of parameters are shown in Table 8. Again bold lines mean the best representation of each system. These revised parameters leave the performance of the model unaf-

fected for glycol ether VLE (as we can conclude when comparing Tables 5 and 8) for all mixtures considered, or improve it, as shown for a typical example in Fig. 8. Detailed deviations for the CPA performance in this system are included in Table 8.

On the other hand, binary LLE is much improved, and good correlation is achieved as shown in Fig. 9 for some systems with a single interaction parameter.

3.4. Second virial coefficient prediction

The prediction of the second virial coefficient through an equation of state is also a strict test of its performance, particularly for multicomponent mixtures. It is well known that virial coefficients are directly related to intermolecular forces and a reasonable representation of virial coefficients from an EoS implies that the model correctly accounts for the interactions between molecules. Classical cubic equations of state do not provide satisfactory second

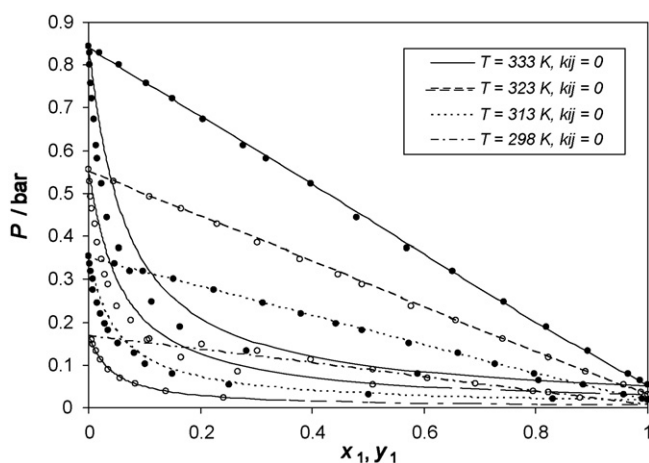


Fig. 8. Comparison between experimental VLE data [31,44] (points) and CPA prediction (lines) for the system C₂E₁ (2B) + methanol using the parameters of Table 7 for the glycol ether and CR1.

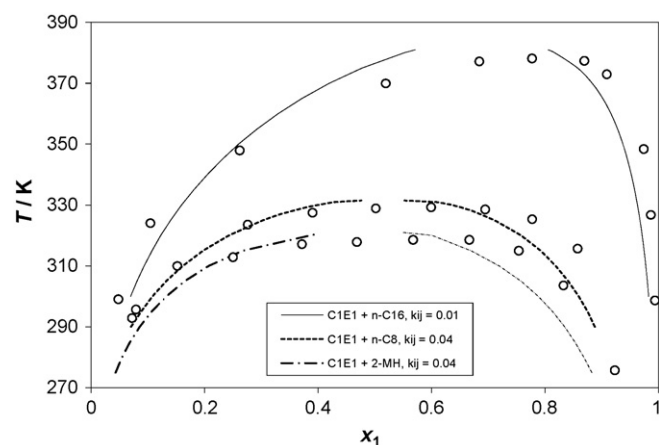


Fig. 9. Comparison between experimental LLE data (points) and CPA correlation (lines) for the system C₁E₁ (2B) + 2-methylhexane [45,46], C₁E₁ (2B) + n-octane [46] and C₁E₁ (2B) + n-hexadecane [47]. The CPA parameters for the glycol ethers are from Table 7.

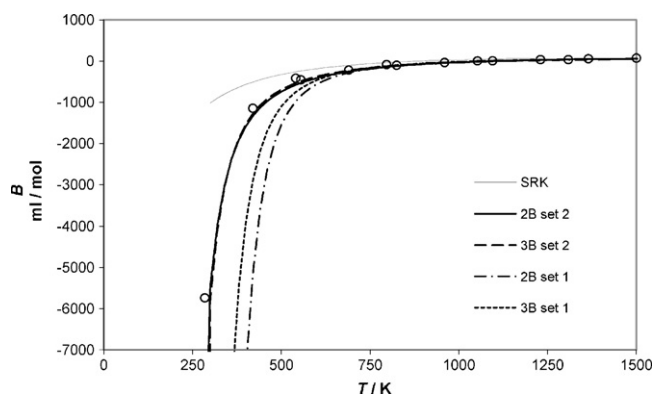


Fig. 10. Second virial coefficient CPA prediction (lines) for C_2E_1 with 2B and 3B association schemes and comparison with experimental data (points) from literature [48,49] and SRK EoS. Set 1 corresponds to the parameters from Table 4 and set 2 to the parameters from Table 7.

virial coefficient predictions, especially at low temperatures, where second virial coefficient values decrease substantially [7].

In the present work, CPA predictions for second virial coefficient are compared to the experimental data, using various sets of parameters. Fig. 10 shows a typical example. We observe that the new set of parameters (from Table 7) also provides better second virial coefficients compared to the first one, from Table 4 (and for both the 2B and 3B schemes). This fact is in agreement with the results showed in Section 3.3.

It was also observed that very satisfactory predictions were generally obtained for C_1E_1 , C_2E_1 and C_4E_1 . Moreover, in all cases the erroneous behaviour of the SRK EoS at low temperatures is corrected. Less satisfactory values are obtained for the more complex surfactants (those with more than one oxyethylene group in the same molecule), but the predictions are still much improved over SRK. It is evident that there is quite some sensitivity in the second virial coefficient prediction on the parameter set used.

3.5. Octanol–water partition coefficient prediction

Finally, Table 9 presents some octanol–water partition coefficients for three surfactants for which experimental data are available (predictions and correlations). It can be shown [50] that at 25 °C the octanol–water partition coefficient is written as:

$$K_{OW} = 0.151 \frac{\gamma_i^{\infty, w}}{\gamma_i^{\infty, o}}$$

where $\gamma_i^{\infty, w}$ and $\gamma_i^{\infty, o}$ are the infinite-dilution activity coefficients in the water and octanol phases respectively. The constant present in the equation depends on the temperature but also on the experimental values of octanol–water solubilities.

Table 9
Octanol–water partition coefficient correlations with CPA for some glycol ethers

Surfactant	Water-phase		Octanol-phase		log K_{OW}^{calc}	log K_{OW}^{exp} [51]
	k_{ij}	$\gamma_i^{w, \infty}$	k_{ij}	$\gamma_i^{o, \infty}$		
C_1E_1	−0.35	0.39	0	1.318	−1.35	−0.77
			−0.117	0.349	−0.77	
C_2E_1	−0.36	2.35	0	1.819	0.10	−0.28
			−0.09	0.6648	−0.28	
C_4E_1	−0.29	2.116	0	0.5087	−0.20	0.80
			−0.125	0.0492	0.80	

The C_1E_1 and C_2E_1 CPA parameters are taken from Table 7 and C_4E_1 ones from Table 4.

In all cases, the k_{ij} for the surfactant–water mixture is taken from experimental data, but that of octanol–surfactant is directly fitted to the octanol–water distribution data, due to lack of data for the binary mixture. The association schemes used for surfactants were 2B for C_1E_1 and C_2E_1 and the 3B scheme for C_4E_1 . The combining rule CR1 was used in all cases except for C_4E_1 + water, where ECR was used, in accordance to the previous phase equilibria calculations.

A negative k_{ij} is required in all cases, and an average value of −0.11 for all octanol–surfactant mixtures considered will lead to an average deviation of 16% in the prediction of the octanol–water partition coefficient.

4. Conclusions

An association model, the CPA equation of state, has been applied to phase equilibria for mixtures of glycol ethers. The model accounts explicitly for hydrogen bonding but a simplified form is used which does not explicitly account for polarity, intramolecular association and does not include a separate treatment of the internal oxygen atoms of glycol ethers.

It has been shown that CPA can correlate (and often also predict) very satisfactorily phase equilibria for mixtures of glycol ethers with alkanes and even associating compounds. Equally satisfactory results are obtained using the 2B and 3B schemes for the glycol ethers. Aqueous mixtures require large interaction parameters and best results are obtained when the 3B scheme is used. The performance of LLE for glycol ether–alkane mixtures can be improved if the co-volume parameter is based on a generalized correlation against the van der Waals volume, while the remaining parameters are fitted to vapor pressure and liquid density data. Moreover both second virial coefficient and octanol–water partition coefficients predictions are improved.

Overall the results are promising but clearly also illustrate difficulties related to the lack, and sometimes uncertainty, of experimental data and limitations of the approach. In terms of data, there is lack of extensive vapor pressure and liquid density data for heavy glycol ethers needed for parameter estimation, spectroscopic data as well as multicomponent data for model validation. Some octanol–water partition coefficients are available, but unfortunately no glycol ether–octanol data are available for estimating the necessary interaction parameter. In terms of the approach followed, the limitations possibly associated to the aforementioned simplifying assumptions are exemplified because different schemes are needed in some cases, closed loop behaviour is described only fairly and is sensitive to interaction parameters, association scheme and combining rules, and simultaneous VLE and LLE description is difficult based on vapor pressures and liquid densities alone and additional considerations are needed. Some of these limitations may be overcome if intramolecular association phenomena are incorporated in the model.

List of symbols

a_0	parameter in the energy term (bar L ² mol ^{−2})
A_i	site A in molecule i
b	co-volume parameter (L mol ^{−1})
B_j	site B in molecule j
B	second virial coefficient
g	radial distribution function
K_{OW}	octanol–water partition coefficient
P	pressure (bar)
R	gas constant (bar L mol ^{−1} K ^{−1})
T	temperature (K)
T_C	critical temperature (K)
T_r	reduced temperature

V_m	molar volume (L mol ⁻¹)
X_{A_i}	fraction of A-sites of molecule i that are not bonded
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i
Z	compressibility factor

Greek letters

a	energy term in the SRK term (bar L ² mol ⁻²)
β	association volume parameter
Δ	association strength
ε	association energy parameter (bar L mol ⁻¹)
η	reduced density
γ^∞	infinite dilution coefficient
ω	acentric factor
ρ	molar density (mol L ⁻¹)

Appendix A. The CPA (Cubic-Plus-Association) equation of state

The simplified CPA EoS, proposed by Kontogeorgis et al. [7,14], can be expressed in terms of pressure, as:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \times \left(1 + \frac{1}{V_m} \frac{\partial \ln g}{\partial (1/V_m)} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i})$$

X_{A_i} is the fraction of A-sites of i which are not bonded and x_i is the superficial mole fraction of component i . X_{A_i} is expressed as:

$$X_{A_i} = \frac{1}{1 + (1/V_m) \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}}$$

$\Delta^{A_i B_j}$ is the association strength between site A on molecule i and site B on molecule j , expressed as follows:

$$\Delta^{A_i B_j} = g(V_m)^{\text{ref}} \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j}$$

where $g(V_m)^{\text{ref}} = (1/(1 - 1.9\eta))$, and $\eta = (1/4V_m)b$

Finally, the energy parameter of the EoS is given by a Soave-type temperature dependency, while b is temperature independent:

$$a(T) = a_0(1 + c_1(1 - \sqrt{T_r}))^2$$

$\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and the association volume respectively. When the CPA EoS is extended to mixtures, mixing rules are required only for the physical term (SRK), while the extension of the association term is straightforward. The classical van der Waals one-fluid mixing and combining rules are used:

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad \text{where } a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad \text{where } b_{ij} = \frac{b_i + b_j}{2}$$

When CPA is used for mixtures of two associating compounds, e.g., alcohols/glycols–water, combining rules for the association energy ($\varepsilon^{A_i B_j}$) and the association volume ($\beta^{A_i B_j}$) are also required. Here, only the CR-1 and the Elliott (ECR) combining rules are presented.

The expressions of the cross-association energy and volume parameters with the CR-1 combining rule are:

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \quad \text{and} \quad \beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}}$$

The expression of the cross-association strength ($\Delta^{A_i B_j}$) with the Elliott combining rule (ECR) is:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}}$$

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