Application of an Association Model to Complex Fluids

Ane S. Avlund, Georgios M. Kontogeorgis and Michael L. Michelsen

Center for Phase Equilibria and Separation Processes (IVC-SEP)
Department of Chemical and Biochemical Engineering
_Technical University of Denmark_
Kgs. Lyngby, Denmark

Introduction

The SAFT equation of state (EoS) was originally proposed thirty years ago, and many versions of SAFT have appeared since then. Most of these versions focus on treating the contributions from the reference fluid and dispersion in different ways, while the association term from the original SAFT papers is used. There are however still several important issues regarding associating fluids which need thorough investigation.

One of these issues is how we should treat large complex associating chemicals. Alcohols, amines, water and glycols have all been more or less satisfactorily modeled with most of the SAFT versions and the time has therefore come to extend the models to compounds with multiple/different functional groups, e.g. alkanolamines or amino acids.

In this work the CPA EoS [1] has been applied to three alkanolamines; monoethanol-amine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA), using a so-called first-level approach where the capabilities of the model have been investigated under certain simplifying assumptions. No special treatment of polarity is used, only the association term of CPA/SAFT is employed. Existing association schemes, like 2B and 4C are used [2] as well as two new schemes within the same framework. No intramolecular association is considered. The structures of the three alkanolamines are shown here with an indication of all sites on hydroxyl and amine groups.

MEA

DEA

MDEA
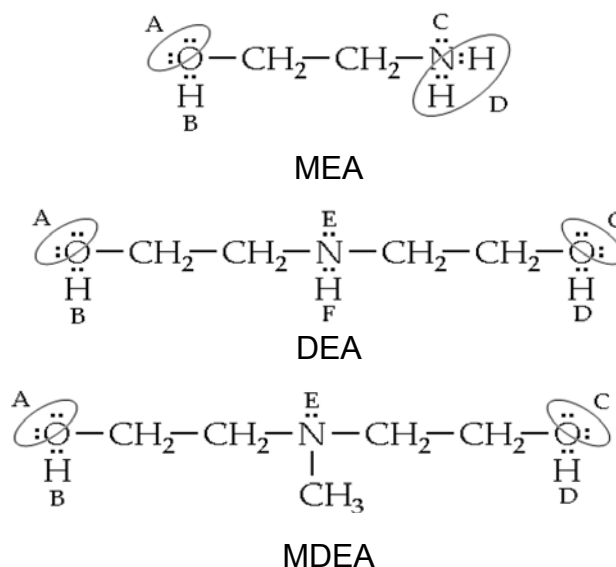
Parameter Estimation

The pure component parameters were at first estimated, in the usual way, from pure component vapor pressure and liquid density data. An often used procedure is to use DIPPR (or other) correlations for the pure component data in the parameter estimation. However, the experimental liquid density data is confined to a narrow temperature range for all three alkanolamines and it was therefore decided to use the actual experimental data in the fitting to avoid transferring errors from the correlations to the parameters.

Different parameter sets can be obtained by fitting only to pure component vapor pressure and liquid density and additional data is therefore needed in order to determine the optimal sets. For MEA and DEA LLE data for binary systems of the alkanolamine and an inert compound was used in this determination, and it was found that this use of LLE data was of imperative importance in the parameter selection. No LLE data was available

for MDEA and Kamlet-Taft solvatochromic parameters [3] were instead used for MDEA. The parameters estimated in this work are shown in Table 1, together with the average relative deviation between CPA and the experimental data.

Table 1: CPA parameters for compounds considered in this work.

Compound	b (L/mol)	$\Gamma=a/(b \times R)$ (K)	c_1	ε/R (K)	$\beta \times 10^3$	ARD%[a] P^s	ARD%[a] ρ_L
MEA 4C	0.05458	2675.1	0.8316	1970.0	13.0	2.22	0.53
MEA 4D	0.05452	2802.9	0.7588	1545.0[b]	10.6[b]	2.89	0.52
				2525.9[c]	8.0[c]		
DEA 4C	0.08964	3582.7	0.9338	2442.4	7.4	4.18	0.40
DEA 6A	0.09010	3471.9	0.911	2010.0	6.8	5.45	0.44
MDEA 4C	0.11249	3132.9	0.7721	2442.4	7.4	1.28	1.71
Water (4C) [4]	0.01452	1017.3	0.6736	2003.2	69.2		
n-Heptane	0.12535	2799.8	0.9137				
Benzene	0.07499	2867.3	0.7576				
Hexadecane	0.29458	3846.4	1.3753				
Methane	0.02985	940.30	0.49811				

[a] ARD% = 1/NP Σ|1-x_i^{CPA}/x_i^{exp}|×100%, [b] amine group, [c] hydroxyl group

Previous work with CPA has shown that alcohols and amines are both best represented using the 2B (1:1) association scheme [5,6] and in accordance with that the 4C (2:2) scheme was investigated for MEA. Alcohols are however known to associate stronger than amines, and the 2B scheme was therefore also investigated, meaning that only the hydroxyl group was considered, while the amine group was ignored. Finally it was investigated whether differentiating between the hydroxyl group and the amine group would improve the results for MEA. The 4 site association scheme with differentiation between the two groups will here be denoted as 4D. The 4D association scheme introduces two additional parameters. To avoid this, the association parameters for the hydroxyl group were found from an approximate average of the association parameters of alkanols [5], while the association parameters for the amine group were estimated to the experimental data already mentioned. In this way the number of variable parameters is the same as for the 4C scheme.

With parameters estimated in this way similar results are obtained for MEA–n-heptane with CPA with each of the three association schemes for MEA. The results with the 2B scheme are however slightly worse than those with 4C and 4D. n-Heptane and other non-self-associating compounds are modeled using CPA, with parameters estimated from pure component vapor pressure and liquid density data.

The parameters were then applied to MEA–benzene. Benzene is non-self-associating but can interact with the associating compounds in a mixture. To account for this the modified CR-1 combining rule (mCR-1) (Folas et al. [7]) is used for this system. mCR-1 includes estimating the cross-association volume β^{AB} between the two components. The results are shown in Figure 1 and the errors are listed in Table 2.

Table 2: Average relative deviation for MEA–benzene between CPA and experimental data

	k_{ij}	β^{AB}	ARD% x_{12}	ARD% x_{21}	ARD% average
2B	0.046	0	24.6	16.4	20.5
4C	0.0058	0.0205	8.4	1.28	4.8
4D	0.0042	0.014	12.0	1.20	6.6

It is clear from Figure 1 and Table 2 that the two 4 site association schemes give significantly better results than the 2B scheme for this system, and that the MEA–benzene LLE is satisfactorily represented by accounting for the solvation in a way similar to that used

for glycols or water with aromatics using the modified CR-1 combining rule when either 4C or 4D is used for MEA. The results with the 2B scheme cannot be improved by accounting for solvation. It is also seen that the 4C scheme gives slightly better results than the more complex 4D scheme.
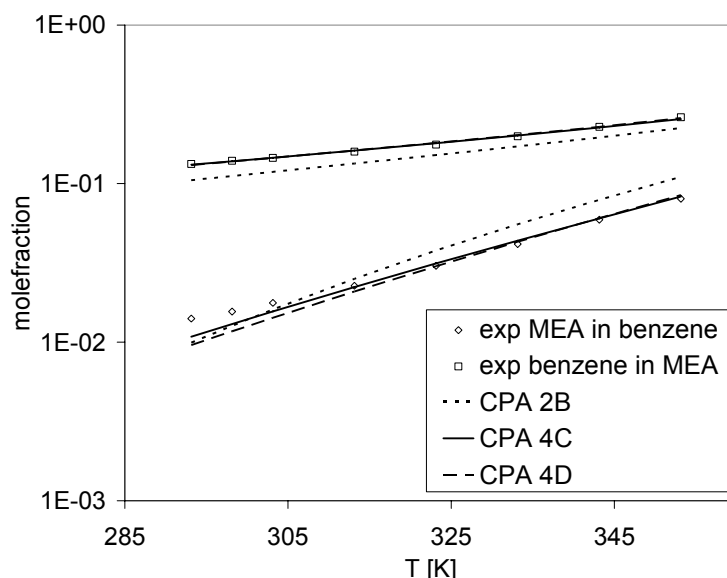
Figure 1: MEA–benzene LLE. Fitted k_{ij} and β^{AB} (the values are listed in Table 1)

The results for MEA–n-heptane and MEA–benzene show that MEA should be assigned 4 sites, meaning that the amine group cannot be ignored. It can also be concluded that the performance of CPA is not improved by differentiating between the association sites on the hydroxyl group and the amine group.

Based on the results for MEA it was decided to investigate two different association schemes for DEA; 4C, where only the association of the two hydroxyl groups is considered while the amine group is ignored, and 6A (3:3) where the hydroxyl groups and the amine group are each assigned 2 sites. There will not be distinguished between different types of sites. The parameters were estimated in a similar way as the MEA parameters, using experimental pure component vapor pressure and liquid density data as well as LLE data for DEA–hexadecane. The results with each of the two association schemes for DEA are shown in Figure 2.
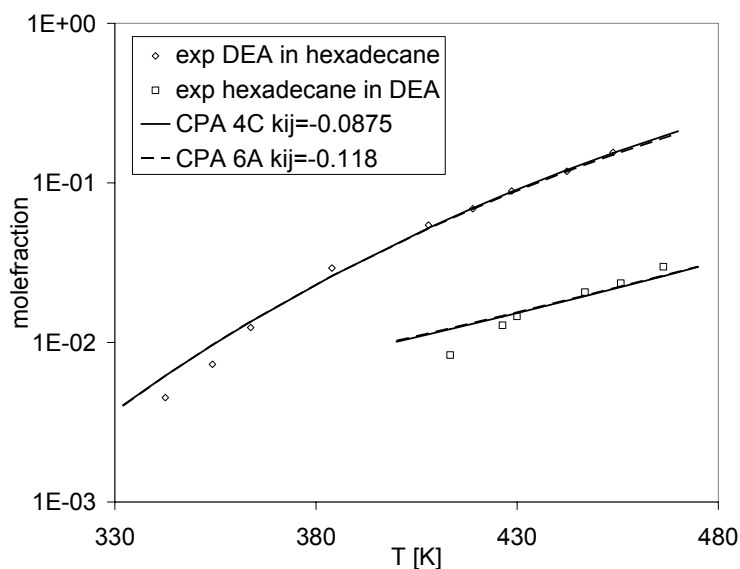

Figure 2: DEA–hexadecane LLE, with an optimal interaction parameter.

The figure shows that the results with the two schemes are very similar, the biggest difference being the value of the optimal interaction parameter. It would be preferable to test the parameters by applying them to a different LLE system, but no more LLE data was found for DEA. The parameters are instead investigated by looking at the VLE of the cross-associating mixture of DEA and water, which will be described in the next section.

MDEA will only be modeled using the 4C scheme, where the ternary amine is ignored. The Kamlet-Taft solvatochromic parameters are a measure of the ability to form hydrogen bonds and the values of the parameters for DEA and MDEA are very similar. This indicates that they associate similarly and because no LLE data was available for MDEA it was decided to apply the 4C association parameters from DEA to MDEA, and fit the remaining three parameters to pure component data.

The MDEA–methane VLE was modeled at five different temperature. Figure 3 shows both the predicted and correlated results with CPA.

The figure shows that CPA predicts ($k_{ij} = 0$) a wrong temperature dependency for this system, and that this is corrected, when a temperature-independent interaction parameter fitted at T = 298.15 K is used, even though the error increases with the temperature.
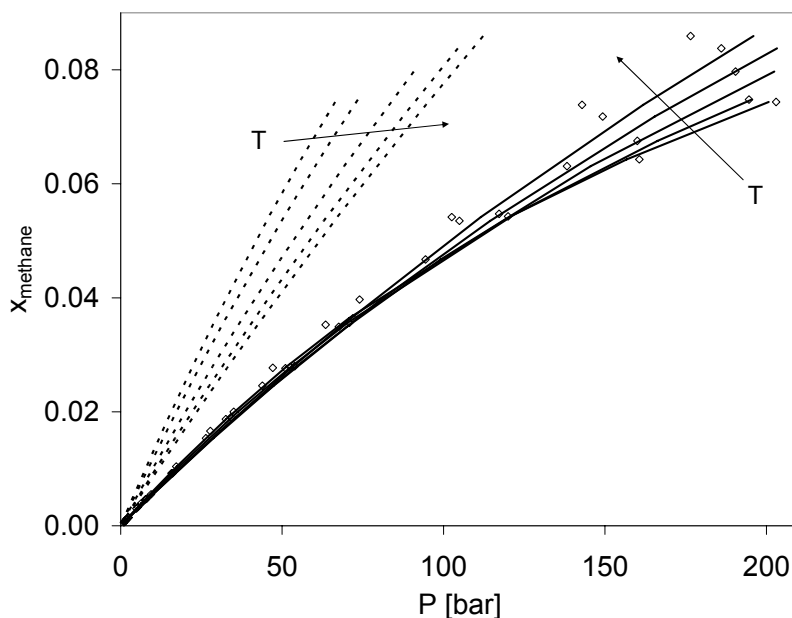

Figure 3: MDEA–methane VLE, at five different temperatures; 298.15 K, 313.15 K, 343.15 K, 373.15 K and 403.15 K. Dotted line: $k_{ij} = 0$, solid line: $k_{ij} = 0.173$.

**Cross-Associating mixtures VLE**

CPA has also been applied to binary VLE cross-associating mixtures containing alkanolamines, especially with water. Figure 4 shows the results for MEA–water with the two 4 site schemes.

Figure 4 shows that CPA satisfactorily correlates this system with both association schemes, and that the two schemes give very similar results, with the same optimal value of the interaction parameter. For both schemes a large negative interaction parameter is necessary in order to model the negative deviation from Raoult's law.
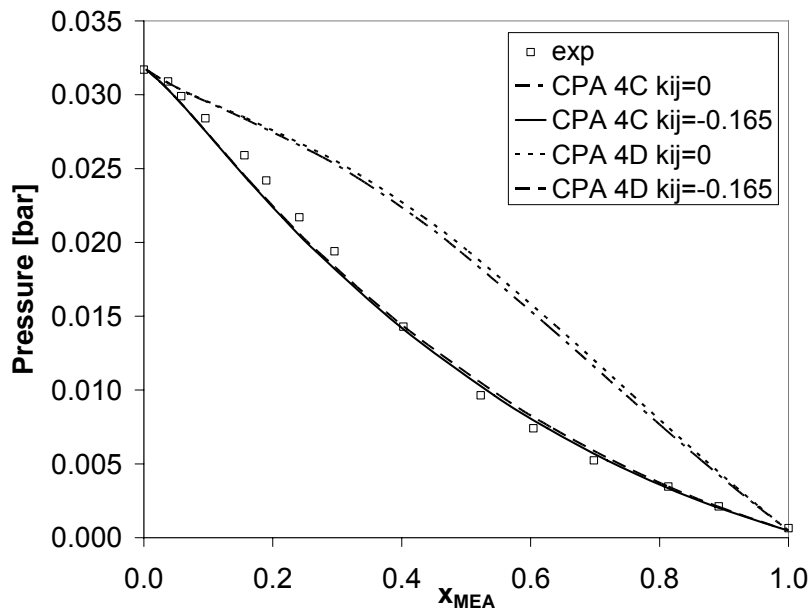
Figure 4: MEA–water VLE at T = 298.15 K.

Figure 5 shows the results for DEA – water at 365.15 K with 4C and 6A for DEA.
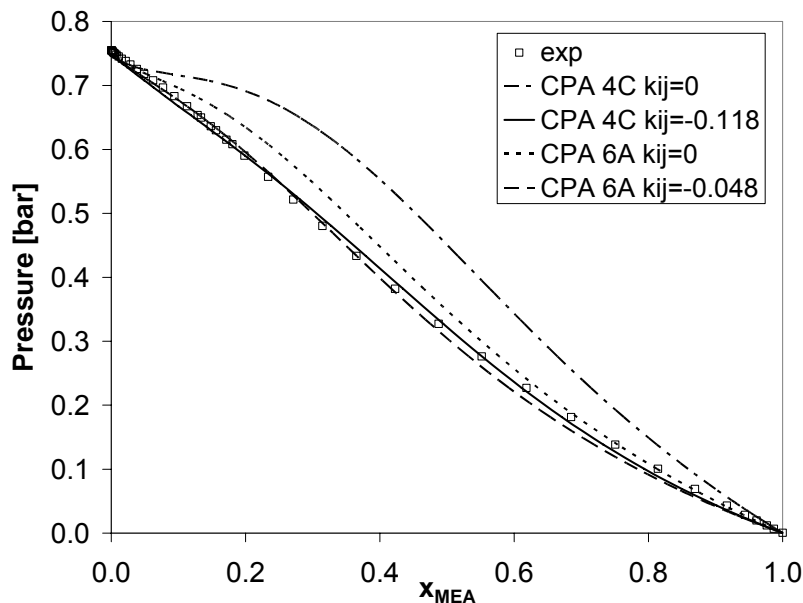
Figure 5: DEA – water VLE at T = 365.15 K.

When looking at the results with a fitted interaction parameter for this system one can again observe that the results with the two DEA schemes are very similar, and that the biggest difference is the value of the optimal interaction parameter. The predictive results with the 6A scheme is better than with the 4C scheme, and a smaller value of the interaction parameter is therefore needed to correct the results.

In general it was found that CPA satisfactorily correlates this type of systems using a temperature-independent interaction parameter. The predictive performance is however poor and large negative values of the interaction parameter are usually needed. These results are in good agreement with results for similar systems previously obtained with CPA [5,6,8], e.g. water-glycol.

Conclusion

The CPA EoS has been applied to three alkanolamines (MEA, DEA, MDEA) as well as to cross-associating mixtures with water and ethanol. The investigation showed that vapor pressures and liquid densities were not sufficient for obtaining reliable parameters, but that at least one other type of information is needed. LLE data for a binary mixture of the associating component with an inert compound is very useful in the estimation.

The 4 site schemes, 4C and 4D proved to be the best choice for MEA The simpler 4C scheme performed as well or better than the more complex 4D scheme, and is therefore recommended for MEA.

The two schemes tested for DEA, 4C and 6A both gave satisfactory and similar results, though different values where needed for the interaction parameter. It is necessary to do more calculations to decide which scheme to recommend.

The 4C scheme performed satisfactorily for MDEA.

A temperature independent interaction parameter gave satisfactory results for LLE and for alkanolamine-water VLE. Large negative values were, however, typically needed for the interaction parameter in the latter case, which is in agreement with previous results for other aqueous cross-associating mixtures, e.g. water-alcohols and water-glycols.

References

[1] G.M. Kontogeorgis, E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, Ind. Eng. Chem. Res. 35 (1996) 4310-4318.

[2] S.H. Huang, M. Radosz, Ind. Eng. Chem. Res., 29 (1990) 2284-2294.

[3] A.F. Lagalante, M. Spadi, T.J. Bruno, J. Chem. Eng. Data, 45 (2000) 382-3

[4] G.K. Kontogeorgis, I.V. Yakoumis, H. Meijer, E. M. Hendrix, T. Moorwood. Fluid Phase Equilibrium, 158-160 (1999) 201-209.

[5] G.K. Folas, J. Gabrielsen, M.L. Michelsen, E.H. Stenby, G.M. Kontogeorgis, Ind. Eng. Chem. Res, 44 (2005) 3823-3833

[6] M. Kaarsholm, S.O. Derawi, M.L. Michelsen, G.M. Kontogeorgis, Ind. Eng. Chem. Res, 44 (2005) 4406-4413

[7] G.K. Folas, G.M. Kontogeorgis, M.L. Michelsen, E.F. Stenby, Ind. Eng. Chem. Res., 45 (2006) 1516-1526.

[8] S.O. Derawi, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Ind. Eng. Chem. Res, 42 (2003) 1470-1477