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Solvation Phenomena in Association Theories with Applications to Oil & Gas and Chemical Industries

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Résumé — Les théories d'association et le phénomène de la solvatation : application aux industries du pétrole et du gaz, et à la pétrochimie — Les théories de l'association issues de la famille des équations SAFT (Self Associating Fluid Theory) expriment explicitement le phénomène de l'auto-association ainsi que de l'association croisée. Ces phénomènes ont une grande importance pratique car ils ont un effet souvent majeur sur l'équilibre de phases de nombreux mélanges d'intérêt industriel. D'un point de vue scientifique, le phénomène de la solvatation est également beaucoup étudié car il intervient dans de nombreux types de mélange, et non seulement ceux contenant des composants auto-associés comme les mélanges de l'eau avec les alcools ou les glycols. Des mélanges ne contenant qu'un seul composé auto-associé, voire aucun, peuvent néanmoins présenter une solvatation spécifique liée à la formation de liaisons hydrogène ou, de manière plus générale, à des interactions de type acide – base de Lewis. Comme exemple, on peut mentionner les mélanges avec un composé polaire (eau, glycol...) et des hydrocarbures aromatiques ou des solutions aqueuses d'éthers ou d'esters.

Ce manuscrit décrit comment le modèle dit "CPA" *(Cubic Plus Association)*, qui contient un terme spécifique pour l'association, issu de l'équation SAFT, peut être utilisé pour rendre compte de différents types d'interactions de solvatation. Le rôle des règles de combinaison dans le terme associatif et les cas où la solvatation doit être traitée explicitement sont illustrés.

Abstract — Solvation Phenomena in Association Theories with Applications to Oil & Gas and Chemical Industries — *Association theories e.g. those belonging to the SAFT family account explicitly for self- and cross-association (solvation) phenomena. Such phenomena are of great practical importance as they affect, often dramatically, the phase behaviour of many mixtures of industrial relevance. From the scientific point of view, solvation phenomena are also very significant because they are present in different types of mixtures and not just those containing two self-associating compounds e.g. water with alcohols or glycols. Mixtures with only one self-associating compound and in some cases even mixtures with two non self-associating compounds may exhibit solvation specifically due to hydrogen bonding or more generally due to Lewis acid-Lewis base interactions. As examples can be mentioned mixtures with polar compounds (water, glycols...) and aromatic hydrocarbons and aqueous ether or ester solutions.*

This manuscript presents how a specific association thermodynamic model, which employs SAFT's association term, the so-called CPA (Cubic-Plus-Association) equation of state, can be applied in order to account for various types of interactions due to solvation. The role of combining rules in the association term and the cases where explicit treatment of solvation is needed will be illustrated.

ABBREVATIONS

CPA	Cubic Plus Association EoS
ECR	Elliott combining rule
EoS	Equation of state
ESD	Elliott-Suresh-Donohue EoS
LA	Lewis acid
LB	Lewis base
LLE	Liquid-liquid equilibria
MEG	Monoethylene glycol
NRTL	Non-random two liquid activity coefficient model
PC-SAFT	Pertubed-Chain SAFT EoS
PR	Peng-Robinson EoS
SAFT	Statistical Associating Fluid Theory EoS
SLE	Solid-liquid equilibria
SRK	Soave Redlich Kwong EoS
VLE	Vapor-liquid equilibria
UNIQUAC	Universal quasichemical theory

INTRODUCTION

There are various types of solvation in mixtures with associating and/or polar compounds, as illustrated in Figure 1. In this context, we will use the term cross-association when both compounds are self-associating *e.g.* mixtures with water and alcohols, and the term solvation when at least one of the compounds cannot self-associate. As illustrated in Figure 1, there are numerous cases of "solvation", some due to hydrogen bonding, others due to Lewis Acid-Lewis Base (LA-LB) interactions in a broader sense, in some cases with one compound being self-associating *e.g.* water-esters and in others with both compounds being "inert" (non self-associating) but capable of solvation *e.g.* chloroform-acetone.

Traditional models like cubic equations of state (EoS) with the van der Waals one fluid mixing rules do not account explicitly for cross-association or solvation phenomena. Only indirectly can the presence of these phenomena be sometimes appreciated using such semi-empirical models. The dominant character in phase equilibria can be sometimes seen *e.g.* via the negative k_{ij} values in strongly solvating systems like water with some alcohols or chloroform-acetone. Classical activity coefficient models like NRTL (Renon and Prausnitz, 1968) or UNIQUAC (Abrams and Prausnitz, 1975) also account implicitly for strong interactions via the values of the interaction parameters. On the other hand, theoretically-derived EoS such as those in the SAFT family have a separate association term and via this term cross-association and solvation phenomena are explicitly accounted for. There are some investigations in the literature for cross-associating/solvating mixtures, but not many systematic studies have been presented with a single model covering various types of cross-association/solvation phenomena present in mixtures. Fu and Sandler (1995) and Wolbach and Sandler (1997, 1998) applied a SAFT EoS to various cross-associating systems (containing acids, water and alcohols), while Li and Englezos (2003, 2004) and Li *et al.* (2006) have applied original SAFT to mixtures containing alcohols, glycols, water and CO_2. Applications of SAFT-VR to cross-associating systems have also been presented (Garcia-Lisbona *et al.*, 1998; Paricaud *et al.*, 2002). The results are satisfactory in these VLE studies, using in almost all cases rather high interaction parameters. Suresh and Beckman (1994) have applied SAFT to water-alcohol-hydrocarbons LLE, while Grenner *et al.* (2006) applied PC-SAFT and ESD (Elliott-Suresh-Donohue) to water-amine-hydrocarbon systems. Further ESD applications for cross associating systems have been presented by Suresh and Elliott (1992). Gross and Sadowski (2002) applied PC-SAFT to water-alcohols. Kleiner and Sadowski (2007) have recently applied PC-SAFT to mixtures with induced solvation.

In this work, we will illustrate that a thermodynamic model using the association term of SAFT can successfully account for different types of cross-association/solvation phenomena, but different considerations may sometimes be needed. We will use a specific simpler version of the SAFT EoS for this purpose, the so-called CPA (Cubic-Plus-Association) EoS which uses an association term similar to SAFT but the physical interactions are accounted for via a simple SRK EoS. No explicit account of polar effects (other than those due to hydrogen bonding) is considered.

CPA is briefly presented in the next section with some references on previous applications of the model to cross-associating and solvating systems. Among the former ones, CPA has been applied to especially water-alcohol and water-glycol mixtures (Kontogeorgis *et al.*, 1999, 2006b; Voutsas *et al.*, 1999; Derawi *et al.*, 2003a; Folas *et al.*, 2005a,b), and from the latter to water with aromatic or olefinic hydrocarbons as well as aromatic perfluorocarbons (Folas *et al.*, 2006a; Oliveira *et al.*, 2007).

1 THE CPA EQUATION OF STATE

The CPA EoS, proposed by Kontogeorgis *et al.* (1996, 1999, 2006a,b), can be expressed for mixtures in terms of pressure P, as:

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

R and T are the ideal gas constant and temperature, respectively.

The key element of the association term is X_A, which represents the fraction of sites A of molecule i that are not bonded with other active sites, while x_i is the mole fraction of component i. X_{A_i} is related to the association strength $\Delta^{A_iB_j}$ between two sites belonging to two different

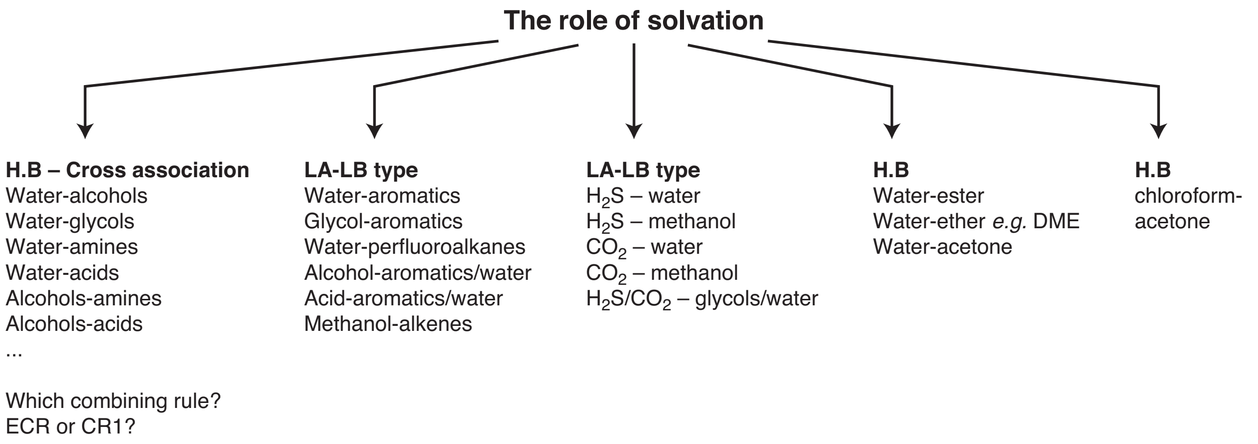

Figure 1

The various types of cross-association and solvation together with some examples, in mixtures containing self-associating (or polar) compounds.

molecules, *e.g.* site *A* on molecule and site *B* on molecule *j*, determined from:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_iB_j}} \tag{2}$$

where the association strength $\Delta^{A_iB_j}$ in CPA is expressed as:

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right) - 1\right] b_{ij} \beta^{A_iB_j} \tag{3}$$

with the radial distribution function $g(\rho) = \frac{1}{1-1.9n}$ and $n = \frac{1}{4} b\rho$ where $b = \sum_i x_i b_i$ which implies that $b_{ij} = \frac{b_i + b_j}{2}$.

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

$$a(T) = a_0(1 + c_1(1 - \sqrt{T_r}))^2 \tag{4}$$

$T_r = \frac{T}{T_c}$ where is the critical temperature.

In the expression for the association strength $\Delta^{A_iB_j}$, the parameters $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are called the association energy and the association volume, respectively. These two parameters are only used for associating components, and together with the three additional parameters of the SRK term (a_0, b, c_1), they are the five pure compound parameters of the model. They are obtained by fitting vapor pressure and liquid density data. For inert (not self-associating) components *e.g.* hydrocarbons, only the three parameters of the SRK term are required, which can be obtained either from vapor pressures and liquid densities or calculated in the conventional manner (critical data, acentric factor *e.g.* as done for gases like CO_2 and H_2S). Table 1 contains a list with the pure compounds parameters of CPA considered in this work.

Alcohols are treated as 2B-site molecules, while water and glycols as 4C, in agreement to previous investigations. For organic acids the 1A-scheme is used. The terminology is from Huang and Radosz (1990).

When CPA is used for mixtures, the conventional mixing rules are employed in the physical term (SRK) for the energy and co-volume parameters. The geometric mean rule is used for the energy parameter a_{ij}. The interaction parameter k_{ij} is, in the applications for self-associating mixtures, *e.g.* alcohol, water, glycol or acid with n-alkanes, the only binary adjustable parameter of CPA:

$$\begin{aligned} a &= \sum_i \sum_j x_i x_j a_{ij} \text{ where } a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \\ b &= \sum_i x_i b_i \end{aligned} \tag{5}$$

For mixtures containing two associating compounds, *e.g.* alcohols or glycols with water, combining rules for the association energy ($\varepsilon^{A_iB_j}$) and the association volume ($\beta^{A_iB_j}$) are required. We use here the CR-1 and the Elliott Combining Rule (ECR) rules, which we have found most successful in previous applications.

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

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \quad \text{and} \quad \beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \tag{6}$$

TABLE 1

CPA parameters for the compounds considered in this work

Table 1a. CPA pure compound parameters for the associating compounds used in this work. Water and DEG are modeled as "4C" molecule, organic acids as "1A", while alcohols are modeled as "2B". The terminology is from Huang and Radosz (1990). The parameters are fitted to vapor pressure and liquid density experimental data by minimizing the absolute average percentage deviations in these two properties. References for the CPA parameters for water, alcohols, acids and DEG are given in the review by Kontogeorgis *et al*. (2006a)

Compound	T_c (K)	b (L mol^{-1})	a_0 (bar L^2 mol^{-2})	c_1	$\varepsilon^{A_iB_i}$ (bar L mol^{-1})	$\beta^{A_iB_i} \times 10^3$
Water	647.29	0.014515	1.2277	0.67359	166.55	69.2
Methanol	512.64	0.030978	4.0531	0.43102	245.91	16.1
Ethanol	513.92	0.049110	8.6716	0.73690	215.32	8.00
2-propanol	508.30	0.064110	10.6019	0.94680	210.00	9.10
n-butanol	563.05	0.079700	15.6949	0.97840	210.00	8.20
n-heptanol	631.90	0.13133	35.73857	1.01096	262.72	0.3
Propanol	536.78	0.064110	11.9102	0.91709	210.00	8.10
Formic acid	588	0.03	5.6336	0.3338	419.17	15.5
Propionic acid	600.8	0.0641	13.2676	0.6891	399.75	2.1
DEG	744.6	0.0921	26.408	0.7991	196.84	6.4
Phenol	694.25	0.0801	18.84	0.9087	174.88	45.3
o-cresol	697.55	0.09583	24.98	0.8960	163.48	26.7
p-cresol	704.85	0.09723	28.84	0.8928	270.03	4.1

Table 1b. CPA pure compound parameters for the inert compounds used in this work

Compound	T_c (K)	a_0 (bar L^2 mol^{-2})	b (L mol^{-1})	c_1
n-nonane	594.60	41.25061	0.16035	1.04628
n-decane	617.70	47.389	0.17865	1.13243
p-xylene	616.23	29.31663	0.1098	0.86256
DnPE	530.60	26.38364	0.11578	0.92963
EPE	500.23	21.76524	0.10034	0.84978
n-butyl acetate	563.80	29.23732	0.11788	1.02499

DnPE = Di-n-propylether
EPE = ethyl propyl ether

and with ECR:

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \tag{7}$$

Thus ECR and CR-1 are similar, the only difference being the second term containing the co-volume parameters in the expression for the cross – association volume.

CPA can be applied to mixtures with one self-associating compound and one inert (*i.e.* non self-associating) compound where there is possibility for solvation between the two compounds. For this purpose, specially suited is the so-called modified CR-1 rule proposed by Folas *et al*. (2006a), which has been applied to mixtures with water or glycols and aromatic or olefinic hydrocarbons. In the modified CR-1 combining rule, we select the energy to be half the value of the energy for the self-associating component, whereas the cross-association volume is teaken as an adjustable parameter regressed from experimental data:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon_{associating}}{2} \text{ and } \beta^{A_iB_j} \text{ (fitted)} \tag{8}$$

Then, the association strength will be estimated by Equation (3) and in this way the in-built temperature dependency of the cross – association strength is retained for solvating systems. Calculations have shown that this is important in order to obtain satisfactory results *e.g.* for water-aromatic hydrocarbons over large temperature ranges.

2 TYPE 1: CROSS-ASSOCIATING MIXTURES

Cross-associating mixtures where both components are self-associating (water, alcohols, amines, glycols, acids, etc.) have been studied extensively with CPA (*e.g.* Kontogeorgis *et al*., 2006b; Folas *et al*., 2005a). An interaction parameter, k_{ij}, is always used for correlating binary phase equilibria.

In these investigations, it has been established that Elliott's rule (ECR) performed best for mixtures of water with light alcohols (methanol, ethanol and propanol) and MEG and CR-1 was superior for water with heavy alcohols and glycols (DEG, TEG, etc.).

Figures 2-7 present a few typical results. The most important conclusions extracted both from these figures and from literature investigations are:

- Choice of combining rules: in many cases especially for size-symmetric systems, the difference is small, but as the asymmetry increases CR-1 performs typically better than ECR *e.g.* for water-heavy alcohols LLE *(Fig. 3)*. This subject has been discussed previously as well (Voutsas *et al.*, 1999; Kontogeorgis *et al.*, 2006b).
- Successful simultaneous correlation of VLE and LLE is difficult for certain systems such as water-butanol. We observe that, when the interaction parameter is fitted to LLE, then prediction of the VLE is not very satisfactory and vice versa. Still CPA can describe, at least qualitatively correct, with the same parameters VLE, LLE and SLE for this system. The ECR is employed in the calculations shown in Figure 2. Even better representation of liquid-liquid can be obtained with the CR-1 combining rule, but ECR is preferred in this case as it performs better than CR-1 in the case of SLE.
- Negative interaction parameter values, k_{ij}, are almost always needed, indicating possibly that the degree of cross-association is underestimated.
- ECR is sufficient for correlating alcohol-alcohol VLE using a small value of the interaction parameter. In agreement to other studies *e.g.* for alcohol-alkanes, small differences are observed in using the 2B or 3B schemes for alcohols *(Fig. 4)*.
- Mixtures of organic acids or amines and alcohols are also successfully modeled using CPA with ECR (Kontogeorgis *et al.*, 2006b, 2007; Kaarsholm *et al.*, 2005), as shown for some typical systems in Figures 5-7, while aqueous mixtures of acids and amines require large negative interaction parameters and the representation is not always entirely satisfactory.

3 CROSS-ASSOCIATING MIXTURES FOR SELECTING OPTIMUM PARAMETERS FOR ASSOCIATING COMPOUNDS

When SAFT-type approaches are used for associating compounds, 5 adjustable parameter sets are usually obtained based on vapor pressure and liquid density data. Several parameter sets can often reproduce the pure compound data within experimental accuracy, as discussed also recently by Clark *et al.* (2006).

One way to select an optimum set is by incorporating mixture data in the parameter selection. The best choice is data of the self-associating compound with an alkane, but as such data is not always available, we will illustrate using the example of alkylphenols, how selection of optimum parameters can be based on cross-associating mixtures.

Phenol and alkyphenols are polar compounds with dipole moments comparable to other polar compounds *e.g.* for phenol the dipole moment is 1.45 (D), for m-cresol it is 1.59 (for comparison, water = 1.85 and methanol = 1.70 D). The

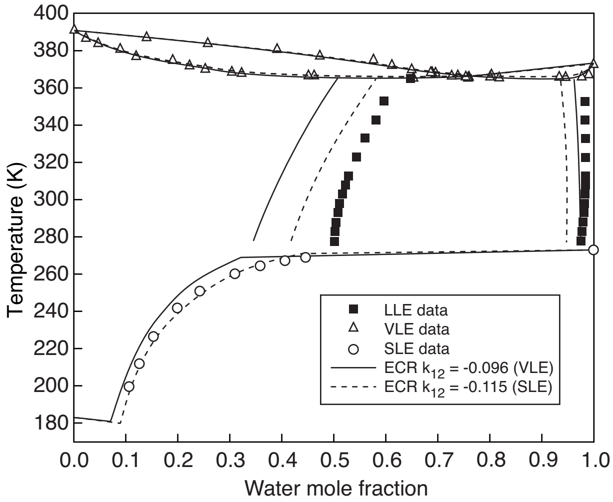

Figure 2

Water/butanol VLE, LLE and SLE using CPA and the Elliott combining rule. The pressure is 1 atm. Experimental data are taken from Sørensen and Arlt (1980), Hessel and Geiseler (1965) and Lohman *et al.* (1997).

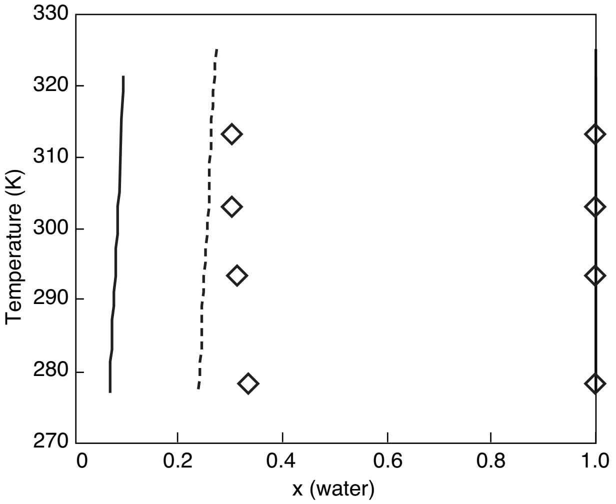

Figure 3

LLE correlation for 1-heptanol-water with CPA and different combining rules. Experimental data from Darwish *et al.* (2002) at 1 atm (◊). CPA calculations with k_{ij} = 0 and with Elliott rule (——) and CR-1 (- - -).

CR-1 performs significantly better than ECR and satisfactory prediction is achieved.

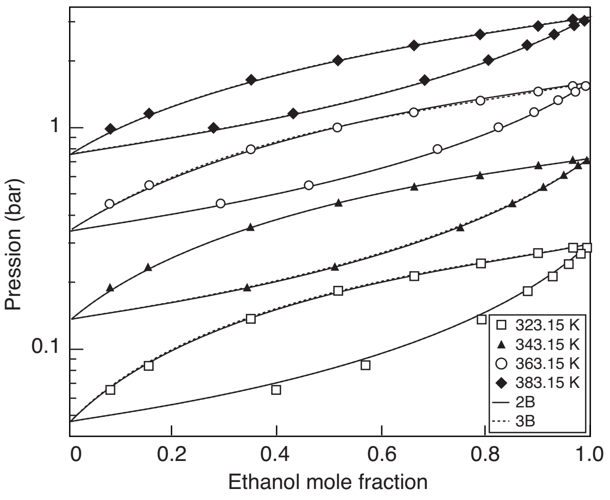

Figure 4

VLE calculations of ethanol-butanol using ECR and the 2B scheme with $k_{ij} = 0.0$ (solid line) or ECR and the 3B scheme with $k_{ij} = 0.0$ (dashed line). Experimental data are from Kharin *et al.* (1969).

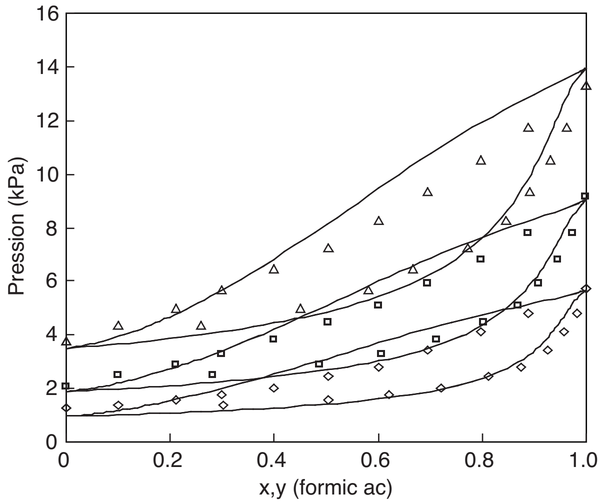

Figure 5

VLE correlation with CPA for the system formic acid-1-butanol. Experimental data from Apelblat and Kohler (1976) at 298.15 K (◊), at 308.15 K (□), and at 318.15 K (Δ). CPA calculations with ECR and $k_{ij} = 0.0651$ at 298.15 K (——), at 308.15 K (——) and at 318.15 K (——).

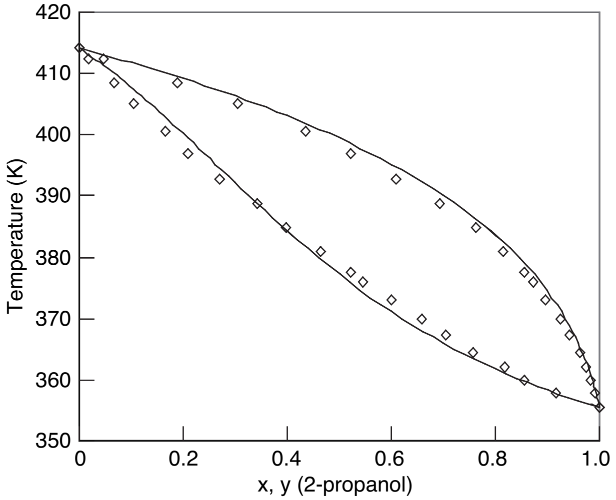

Figure 6

VLE correlation for the system 2-propanol-propionic acid. The pressure is 1 atm. Exp. data from Amer-Amezaga (1975) (◊). CPA with CR-1 rule, $k_{ij} = -0.0648$ (——).

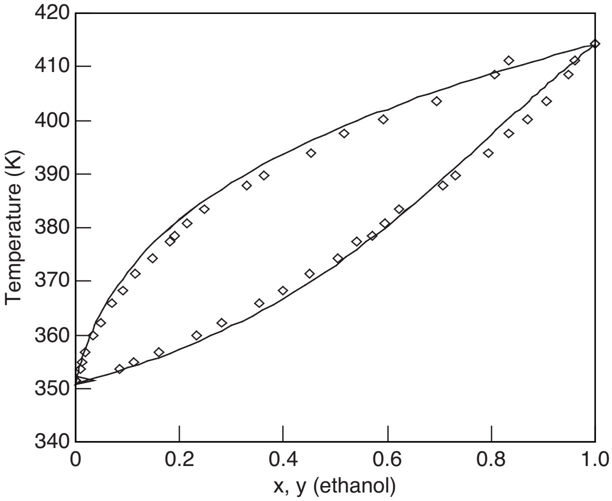

Figure 7

VLE correlation for the system ethanol-propionic acid. The pressure is 1 atm. Exp. dat from Amer-Amezaga (1975) at 101.32 kPa (◊) and CPA calculations with CR-1 and $k_{ij} = -0.0547$ (——).

phenol and alkylphenol compounds can, in principle, be modeled with the same association scheme as for alcohols (the 2B scheme), which is in agreement with the fact that they form linear oligomers. Both phenol and alkylphenols were considered here. The pure compound parameters for phenol and o- and p-cresol are presented in Table 1, while Table 2 presents various parameter sets for m-methylphenol (m-cresol). This alkyphenol is chosen for a deeper analysis, as several data is available. For details on the parameter estimation, see the heading of Table 2.

We hereafter discuss in more detail the investigations regarding m-cresol. As can be seen in Table 2, essentially all sets correlate vapor pressure and liquid density very well, thus the final choice could be based on other properties and

TABLE 2

CPA pure compound parameter sets and average deviations for m-cresol

The different sets of parameters are initially obtained from the correlation of the experimental vapor pressure and liquid density data in the reduced temperature range: 0.5-0.9. Parameter sets 1 and 1b are obtained by fixing the value of the co-volume parameter, *b*, during the estimation procedure (two different values based on the correlation of co-volume with the van der Waals volume). In the case of parameter sets 4 and 4b, the co-volume and the association energy ($\varepsilon^{A_iB_i}$) are fixed (again with two different values of the co-volume parameter). And finally, for parameter set 2 the association energy was fixed while for parameter sets 3 and 7 none of the parameters were fixed.

Set	a_0 (bar L^2 mol^{-2})	b (L mol^{-1})	c_1	$\varepsilon^{A_iB_i}$ (bar L mol^{-1})	$\beta^{A_iB_i}$	ΔP (%)	$\Delta\rho$ (%)
1	28.411	0.09754	0.82074	200.08	0.0067	0.11	0.55
2	28.821	0.09757	0.93141	170.00	0.0068	0.39	0.58
3	28.459	0.09769	0.82413	199.30	0.0067	0.13	0.52
4	28.825	0.09754	0.93181	170.00	0.0067	0.39	0.59
7	25.500	0.09651	0.65073	248.71	0.0086	1.16	0.75
1b	28.709	0.09884	0.83382	197.65	0.0068	0.21	1.25
4b	28.718	0.09884	0.92336	170.00	0.0093	0.54	1.27

$$\text{where } \Delta P(\%) = 100x\frac{1}{NP}\sum_{1}^{NP}\frac{\left|P^{\exp}-P^{calc}\right|}{P^{\exp}} \text{ and } \Delta\rho(\%) = 100x\frac{1}{NP}\sum_{1}^{NP}\frac{\left|\rho_{\exp}-\rho_{calc}\right|}{\rho_{\exp}}$$

mixture data. From spectroscopic data (Kziazckzac and Moorthi, 1985), the enthalpy of hydrogen bonding is 2096 K, which is closer to sets 2, 4 and 4b (2% deviation) and 1, 3, 1b (14% deviation) but somewhat different from set 7 (40% deviation).

In principle, mixture LLE data for m-cresol with alkanes could be useful for choosing the best parameter set, but as such data is not available, an initial investigation could be based on VLE data with alkanes. Table 3 summarizes the results and it can be clearly seen that the performance of CPA in describing these mixtures is very satisfactory, irrespectively of the parameter set used for m-cresol.

LLE data for cross-associating mixtures can be also used for parameter investigation. LLE data for m-cresol with water are available from various sources (Leet *et al*., 1987; Sidgwick *et al*., 1915; Pfohl *et al*., 1997; Varhanickova *et al*., 1996).

For each parameter set, the LLE of m-cresol with water has been studied considering both combining rules, ECR and CR-1. The results are presented in terms of average deviations in Table 4 together with the binary interaction

TABLE 3

Average deviations of pressure and vapor compositions with different sets of parameters for m-cresol(1)-alkanes(2). NP is the number of experimental data points

Comp. 2	T (K)	NP	Set	k_{ij}	ΔP (%)	$\Delta y \times 100$	Ref. to exp. data
Methane	462, 542	14	1	–0.034	3.2	0.37	Simnick *et al*. (1979)
			3	–0.0326	3.1	0.37	
			7	–0.0019	5.3	0.71	
			1b	–0.0219	2.8	0.37	
n-nonane	373, 413	33	1	0.0062	2.3	0.53	Niederbroecker *et al*. (1997)
			3	0.0066	2.4	0.54	
			7	0.0075	2.2	0.75	
			1b	0.009	2.4	0.54	
n-decane	373, 433	29	1	0.0017	2.2	0.80	Schmelzer *et al*. (1996)
			3	0.0021	2.3	0.80	
			7	0.0059	3.5	1.53	
			1b	0.0045	2.3	0.79	

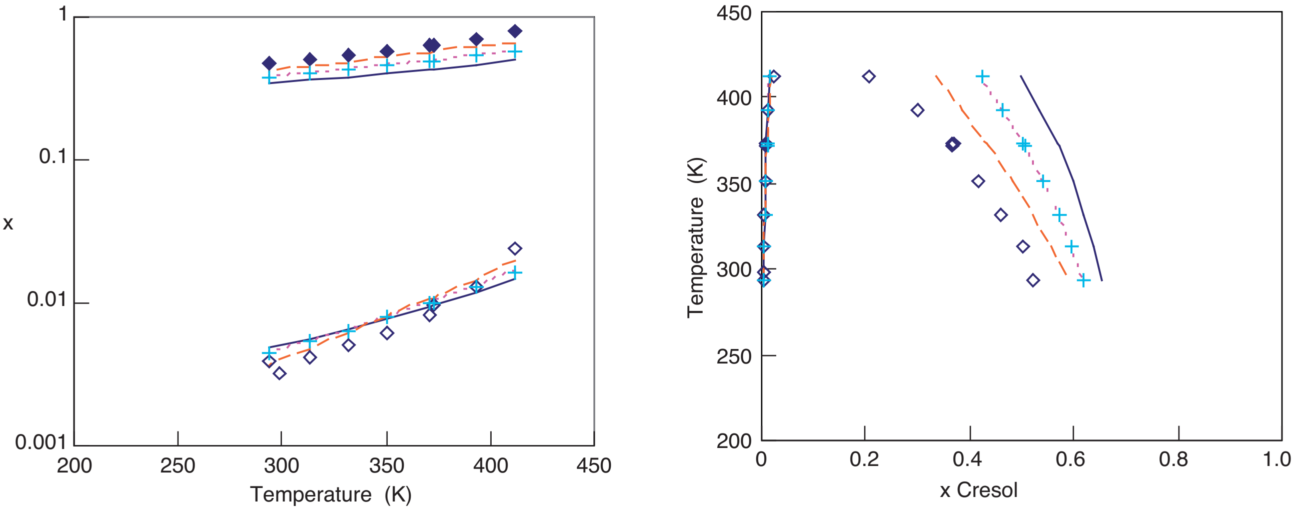

Figure 8.

(Left) LLE with CPA for the binary water (1)-m-cresol (2). Composition of water in the organic phase, x_1^{II} (♦) and composition of m-cresol in the aqueous phase, x_2^{I} (◊). CPA calculations with CR-1 and different parameter sets: set 1 (----), set 2 (——), set 3 (+) and set 7 (– – –). (Right) LLE with CPA for the binary water (1) – m-cresol (2) (◊). CPA calculations with CR-1 and different parameter sets: set 1 (----), set 2 (——), set 3 (+) and set 7 (– – –). The interaction parameters correspond to those of Table 4.

TABLE 4

Average deviations of compositions with different sets of parameters for m-cresol (1)-water(2) with CPA using the ECR and CR-1 combining rules

Set	CR	k_{ij}	Δx_1^{II} (%)	Δx_2^{I} (%)
1	ECR	–0.05	52.1	19.9
	CR-1	–0.032	21.9	18.6
2	ECR	–0.0488	61.4	22.4
	CR-1	–0.0324	31.2	21.6
3	ECR	–0.505	52.3	20.10
	CR-1	–0.033	22.0	18.7
4	ECR	–0.0487	61.6	22.4
	CR-1	–0.0323	31.4	21.7
7	ECR	–0.064	39.5	19.5
	CR-1	–0.0446	12.1	16.9
1b	ECR	–0.0545	52.4	20.5
	CR-1	–0.037	21.8	18.8
4b	ECR	–0.053	58.0	21.9
	CR-1	–0.0363	27.3	20.7

parameters obtained. A sample result is shown in Figure 8 (with some of the parameter sets).

From the table above, it is, first of all, clear that the CR-1 rule provides much better correlation of the experimental data than the Elliott combining rule. In all of the cases, the average deviations are significantly smaller, as are the values of the binary interaction parameters. Besides this, it seems that four of the parameter sets can be pointed out as being superior to the rest, these are sets 1, 3, 1b and 7, for which the average deviations are clearly smaller than for the other sets. Set 1 of Table 2 is overall the most appropriate for m-cresol, considering all properties, including the LLE data with water.

4 TYPE 2: INDUCED SOLVATION

We use the term “induced solvation” when only one of the compounds is self-associating but can “chemically” interact with another compound. This is a widely used term to characterize all types of solvations, either specifically due to hydrogen bonding or in more general terms of Lewis acid-Lewis base interactions. Especially the latter type of interactions, evidently present in mixtures of water or glycols with aromatic hydrocarbons (to a lesser extent also with olefinic hydrocarbons), have been successfully modeled previously with CPA using the modified CR-1 rule (Folas *et al*., 2006a). The solvation can explain the higher solubilities of MEG in the toluene (compared to heptane) in water. Equally higher due to solvation are the solubilities of aromatic hydrocarbons in water, compared to their corresponding alkanes.

A typical example is shown in Figure 9 for water-p xylene.

Mixtures of alcohols or acids with aromatic hydrocarbons also exhibit some solvation, but its significance is less important in applications with CPA (Folas *et al*., 2006a;

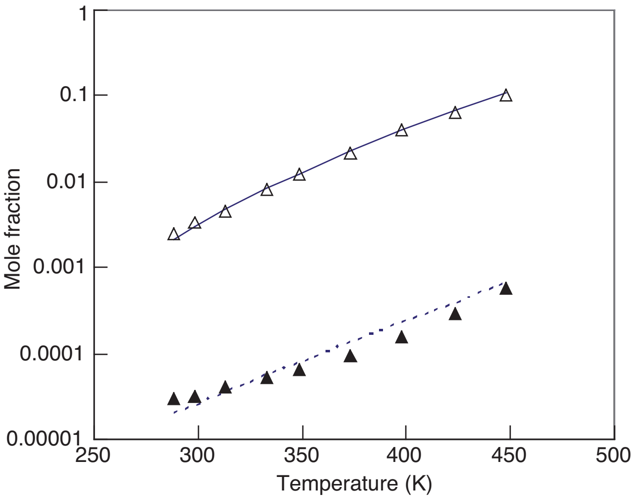

Figure 9

LLE with CPA for the system water (1)-p-xylene (2), x_1^{II} (Δ) and x_2^{I} (▲). CPA calculations considering solvation: k_{ij} = –0.0133 and = 0.0667, x_1^{II} (——) and x_2^{I} (- - -). Exp. data from Jou and Mather (2003).

Kontogeorgis *et al*., 2007). This may be due to the fact that such mixtures are miscible and VLE calculations are often less sensitive to detailed molecular representation.

A very challenging task where induced solvation is present are mixtures of water and highly polar compounds like ketones *e.g*. water-acetone. One way to describe such mixtures with association theories is to treat acetone as self-associating compound (using the 2B scheme), and this approach has been successfully implemented in both PC-SAFT (von Solms *et al*., 2004) and CPA (Folas *et al*., 2006b). In this way, satisfactory results are obtained for both water-acetone VLE and acetone-hydrocarbon VLE, including the azeotropic behaviour of the latter. Naturally, this approach is semi-empirical, as ketones, strictly speaking, are not self-associating compounds.

In this section, we will investigate the importance of explicitly accounting for induced solvation due to hydrogen bonding. We will consider two cases of practical importance to the petroleum and chemical industries: acid gases in mixtures with polar compounds and aqueous solutions with ethers and esters.

4.1 Acid Gases

Mixtures with acid gases (CO_2 and H_2S) are very important in petroleum applications as well as in the chemical industry.

Some investigations of such mixtures with CPA-like EoS have been previously reported in the literature. Perakis *et al.* (2006, 2007) and Voutsas *et al.* (2007) have applied a PR-CPA to several VLE systems containing CO_2: CO_2-water-ethanol, CO_2-water-acetic acid and CO_2 with various polar compounds (acetone, diethyl ether). They obtain good results by treating CO_2 as a self-associating molecule (with 4 sites). They use the geometric-mean rule for both the cross-association energy and volume parameters, thus using a combining rule which is different than both ECR and CR-1 rules. Ruffine *et al.* (2006) have used CPA (in the same form as in *Section 1*) for VLE of binary H_2S mixtures (with water, methanol and alkanes). Satisfactory results are obtained when H_2S is treated as self-associating molecule and using yet another choice for the combining rules for the cross-associating parameters: the geometric mean rule for the energy and the arithmetic mean rule for the volume.

Folas *et al.* (2006b) modeled CO_2-water VLE, treating CO_2 as inert compound and using a k_{ij} = –0.066 optimized from data within the range 298-318 K. Such a simplified approach provided satisfactory representation of CO_2-water VLE at all temperatures and in general, as also shown by Kontogeorgis *et al.* (2006b), CPA correlates well the CO_2 solubility in water over extensive pressure ranges. Folas *et al.* (2006b) investigation on CO_2-water was an intermediate step in their subsequent study of multicomponent mixtures with CO_2 (and N_2), water and dimethyl ether.

All the above investigations of CO_2 and H_2S contain some degree of approximation as in reality CO_2 and H_2S are non self-associating molecules, but on the other hand they can solvate with water and the lower molecular weight alcohols, especially methanol. Not accounting for the solvation yields poor description of the water solubility in CO_2 as shown in figure 10 (also Kontogeorgis *et al.*, 2006b).

Satisfactory results are obtained if we account explicitly for the solvation in mixtures between CO_2-water and H_2S-water (exactly as previously mentioned for water or glycols with aromatic hydrocarbons), at the cost of an additional adjustable parameter. In this way, satisfactory results are obtained, also for the water solubility in CO_2 at very high pressures *(Fig. 10)*. The same is true for H_2S-water, as shown in Figure 11.

Mixtures with alcohols, glycols and phenols have been also investigated. A few examples are shown in Figures 12-14.

The conclusion is that solvation is of importance and yields better results with CPA for mixtures of CO_2 or H_2S with small alcohols, particularly methanol and ethanol, but is of much lesser or no importance for heavier alcohols (propanol, etc.), phenols or glycols.

This could be anticipated from an analysis of the Kamlet-Taft parameters (α, β), which are measures of the bacisity and acidity of compounds. CO_2 is a rather strong base with a "β" parameter around 0.45-0.47 (Walsh *et al.*, 1987) and is thus expected to solvate stronger with

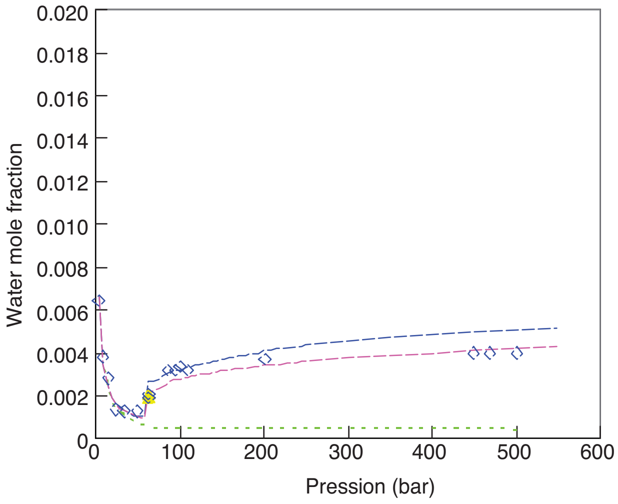

Figure 10

Prediction (k_{ij} = 0) with CPA of the water (4C) solubility in CO_2 assuming solvation between water and CO_2 at T = 298.15 K [blue (dashed) and pink (full) lines; k_{ij} = 0.0, $\beta^{A_iB_j}$ = 0.06 or k_{ij} = 0 and 5% solvation]. The green (dotted) line shows the results when no solvation is assumed and with a k_{ij} value (–0.066) obtained from CO_2-water VLE data. Experimental data are from Gillespie and Wilson (1982).

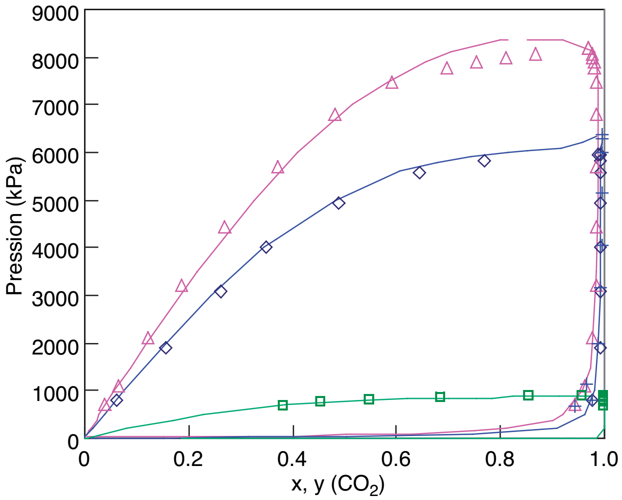

Figure 12

VLE with CPA for the system CO_2-methanol. CPA correlation with critical properties and solvation (2 sites) for CO_2, with k_{ij} = 0.0384 and $\beta^{A_iB_j}$ = 0.01998 at 230 K (——), at 298 K (——) and at 313 K (——). The experimental data are at 230 K (□) from Hong and Kobayashi (1988), at 298 K (◇) from Ohgaki and Katayama (1976) and at 313 K (△) from Yoon *et al*. (1993). Without accounting for the solvation, a k_{ij} = –0.0051 is required but the representation is not as satisfactory as when solvation is explicitly accounted for.

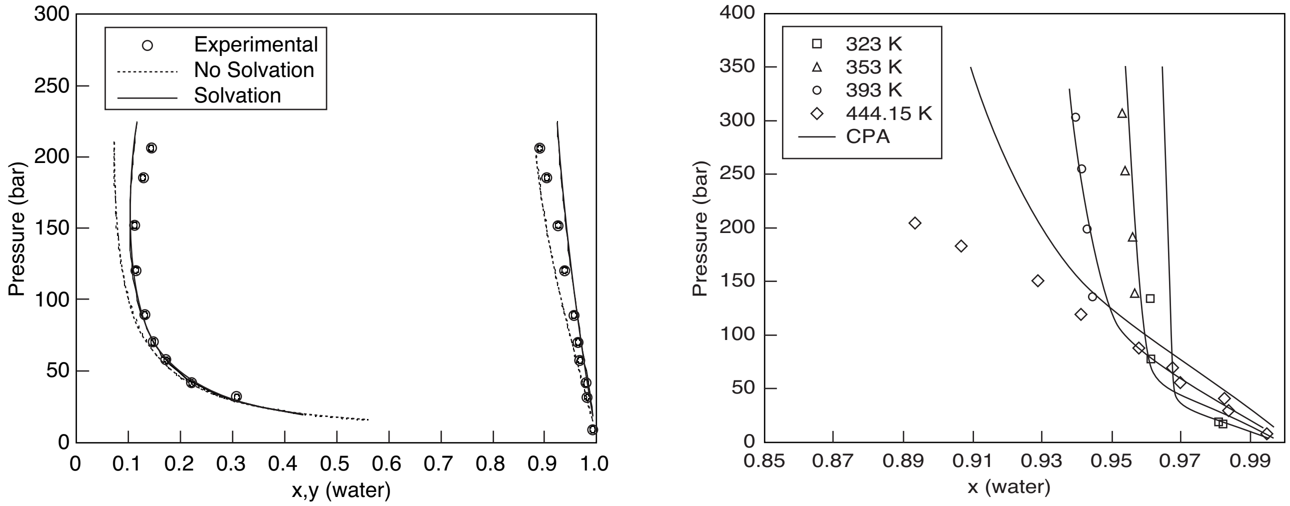

Figure 11

VLE with CPA for the system water-H_2S at 444.15 K. (Left) Experimental data are from Selleck *et al*. (1952) and CPA calculations using two different approaches, without accounting for solvation and accounting explicitly for solvation using Equation (8). (Right) Experimental data from Selleck *et al*. (1952) and Koschel *et al*. (2007) and CPA calculations using only the solvation approach at different temperatures.

"stronger acids" like water (1.17, 0.18) and methanol (0.93, 0.62) than with ethanol (0.83, 0.77) or even propanol (0.78, 0.86). The values in parentheses are, respectively, the Kamlet-Taft acid and base parameters (Kamlet *et al*., 1983).

As illustrated in Figure 15, CPA can correlate CO_2-glycol phase equilibria without need to account explicitly for the solvation. Similar results have been obtained for other mixtures as well *e.g*. CO_2-MEG, CO_2-phenol and methyphenol and H_2S-DEG.

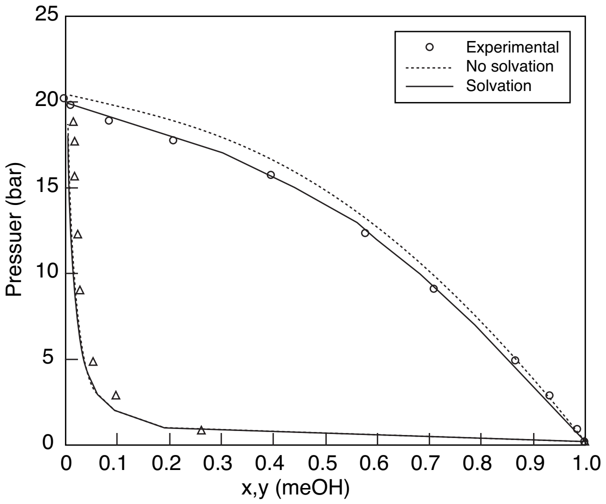

Figure 13

VLE with CPA for the system methanol-H_2S at 298.15 K. Experimental data from Leu *et al*. (1992). Without solvation $k_{ij} = -0.04$; with solvation $k_{ij} = 0.0$, $\beta^{A_iB_j} = 0.05$.

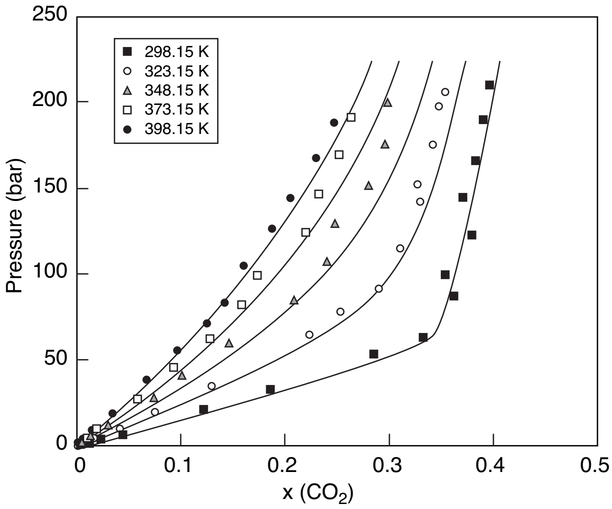

Figure 14

VLE prediction ($k_{ij} = 0$) of CO_2-DEG using CPA.

4.2 Aqueous Mixtures with Esters and Ethers

LLE data are available for certain polar compounds like ethers and esters with water. Figures 15-17 show a few typical calculations but similar results have been obtained for other ethers and esters in water.

Ethers and esters are treated as inert compounds without explicitly accounting for the polarity.

Strong solvation and increased solubility are expected in these mixtures due to the presence of a polar compound in a mixture with water. In these cases, it is sufficient to account for the solvation using the modified CR-1 combining rule. When solvation is accounted for, excellent results are obtained.

The major conclusions from the analysis of the results illustrated in Figures 15-17 and pertinent calculations are:

- The need of explicitly accounting for the solvation is apparent as without it, the predicted solubilities are much lower than the experimental data, thus k_{ij} values which have high and negative values are required and moreover even when interaction parameter is used LLE cannot be appropriately modeled (*e.g*. in Figure 15 the experimental solubility of water in the organic phase is higher than the solubility of DPE in aqueous phase, the model predicts the opposite solubility behavior).

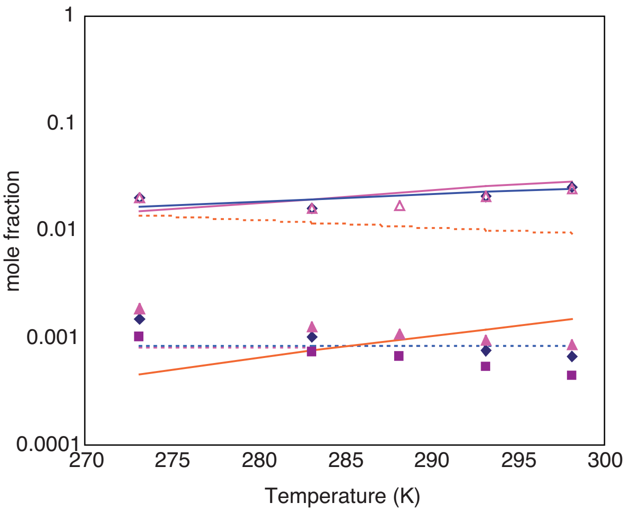

Figure 15

LLE for the system DPE-water (Sørensen and Arlt, 1980): Mole fraction of water in organic phase (◇, △) and of DPE in aqueous phase (◆, ▲, ■). CPA calculations with: a) 1 site solvation, $k_{ij} = -0.1769$ and $\beta^{A_iB_j} = 0.196$: water in organic phase (——) and DPE in aqueous phase (– – –). b) 2 site solvation, $k_{ij} = -0.177$ and $\beta^{A_iB_j} = 0.0555$: water in organic phase (——) and DPE in aqueous phase (– – –). c) No solvation, $k_{ij} = -0.328$: water in organic phase (——) and DPE in aqueous phase (– – –).

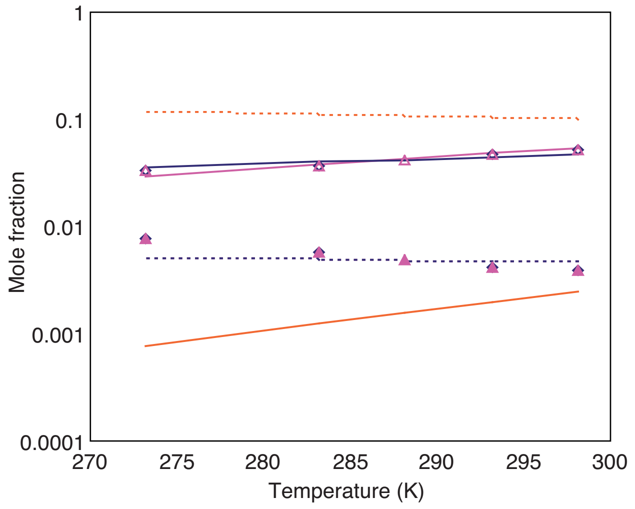

Figure 16

LLE for the system EPE–water (Sørensen and Arlt, 1980): Mole fractions of water in organic phase (◊, △) and of EPE in aqueous phase (♦, ▲). CPA calculations with: a) 1 site solvation, $k_{ij} = -0.1914$ and $\beta^{A_iB_j} = 0.2617$: water in organic phase (——) and EPE in aqueous phase (- - - -). b) 2 sites solvation, $k_{ij} = -0.1931$ and $\beta^{A_iB_j} = 0.0697$: water in organic phase (——) and EPE in aqueous phase (- - - -). c) No solvation, $k_{ij} = -0.4909$: water in organic phase (——) and EPE in aqueous phase (- - - -).

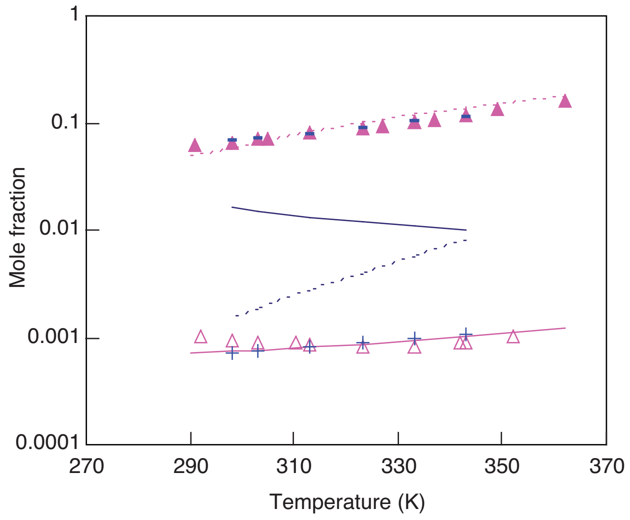

Figure 17

LLE (data from from Sørensen and Arlt (1980)) for the system water (1)-n-butyl acetate (2): mole fraction of water in n-butyl acetate (▲) and mole fraction of n-butyl acetate in water (△). CPA calculations without solvation and $k_{ij} = -0.302$: x_1^{II} (- - - -) and x_2^{I} (——). CPA calculations with 1 site solvation, $k_{ij} = -0.124$ and $\beta^{A_iB_j} = 0.304$: x_1^{II} (- - - -) and x_2^{I} (——) and 2B solvation, $k_{ij} = -0.119$ and $\beta^{A_iB_j} = 0.086$: x_1^{II} (–) and x_2^{I} (+).

TABLE 5

Kamlet-Taft Solvatochromic parameters for some compounds (From Kamlet *et al*., 1983)

Compound	Base parameter, β	Acid parameter, α
DiPE	0.49	0.0
DBE	0.46	0.0
DEE	0.47	0.0
DPE	0.46	0.0
Ethylacetate	0.45	0.0
Methylacetate	0.42	0.0
Toluene	0.11	0.0
Benzene	0.10	0.0
Methanol	0.62	0.93
Ethanol	0.77	0.83
MEG	0.52	0.90
water	0.18	1.17
acetone	0.48	0.08
chloroform	0.00	0.44
CO_2	0.45-0.47	0

- Equally satisfactory results are obtained whether either the 1-site type or 2-site type solvation scheme are being used (*i.e*. 1 or 2 solvating sites in the O atom of ethers or esters), though somewhat better results in the latter case. The 1-site scheme has been investigated as it is consistent with the representation of alcohols, discussed previously, which are described using the 2B scheme *i.e*. one site for both lone pair electrons in the O atom.
- VLE of ether or ester-water is also improved when solvation is accounted for. However, for VLE description of ethers or esters with other self-associating compounds (alcohols, acids) solvation is not as important and can be ignored.

CONCLUSIONS

We have investigated with CPA several of the cross-associating/solvating mixtures summarized in Figure 1, and Table 5 provides the acid/base Kamlet-Taft solvatochromic parameters for some of the compounds studied here. These parameters offer a way to quantify the expected solvation phenomena.

The following points summarize the most important conclusions from the extensive study of CPA to several solvating systems:

1 CPA (in general SAFT-type approaches) can explicitly account for the different types of cross-association and solvation phenomena.

2 For cross-associating mixtures, ECR can be used for mixtures with compounds having relatively small size difference such as water with methanol – propanol, while CR-1 should be preferred for size-asymmetric mixtures. Satisfactory results are obtained over extended temperature ranges.

3 The modified CR-1 combining rule is a successful way for accounting for the induced solvation present in many mixtures.

4 The strongest LA/LB type solvation is observed when "highly associating" compounds like water and glycols (4C-type molecules) are present (together with aromatic, olefinic or perfluoro aromatic-hydrocarbons). In these cases, LLE data is available and the solvation should be always accounted for.

5 For LA/LB or hydrogen bonding solvation where only VLE data is available, the solvation seems to be far less important and can be ignored. This includes alcohols or acids with aromatics.

6 For the solvating hydrogen bonding systems *e.g.* water with ethers or esters, the solvation is always very strong and cannot be neglected.

7 In most solvating systems *e.g.* water with aromatic hydrocarbons or aqueous ester and ether solutions, two adjustable parameters have been used, one in the physical (SRK) and one in the association term. It is not as yet fully investigated whether one of these parameters could be obtained from other than mixture phase equilibrium data.

8 All these conclusions seem to be in agreement with the Kamlet *et al.* solvatochromic parameters. For example, water and glycols with a very acid parameter solvate with basic compounds like aromatic hydrocarbons and also with the strong basic ethers and esters. The same is the case for the interaction of a strong LA (chloroform) with a strong LB (acetone) or CO_2 (base) and water or methanol (high acid values). Methanol is a strong LA but also a strong LB thus its interaction with basic compounds is somewhat less pronounced compared to compounds which are "mostly acidic" like water or MEG.

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