# A Statistical Associating Fluid Theory Perspective of the Modeling of Compounds Containing Ethylene Oxide Groups

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ABSTRACT: Compounds containing ethylene oxide groups as a repeating unit, such as glycols and their ethers, have several applications across different industrial fields. For efficient simulation, design, and optimization of industrial processes based on these compounds, reliable and robust thermodynamic models able to accurately describe their phase equilibria and thermophysical properties are required. For the choice of thermodynamic models available in the literature, the selection of the most adequate is not always obvious, but results have shown overtime that, for associating or polar fluids, association models derived from the statistical associating fluid theory are more accurate and physically sound than the cubic equations of state widely used by industry. However, the current modeling approaches used within the framework of association models have known limitations that must be understood by those developing and applying these models as they often result in a loss of accuracy and extrapolative or predictive ability. This review provides a literature survey of the different works on the modeling of compounds containing ethylene oxide groups using association models, discussing their capabilities and limitations while giving a perspective for future developments in this field.
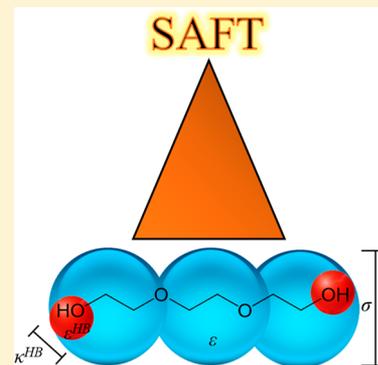
1. INTRODUCTION

Glycols, whose general chemical formula is given by H-(O-CH$_2$-CH$_2$)$_n$-OH, are polyethers with two hydroxyl end-groups having ethylene oxide (EO) as a repeating unit. They are characterized by interesting properties such as their high boiling points, hygroscopicity, noncorrosiveness, freezing point depression of aqueous solutions, low viscosity, and lubricating and plasticizing character, having many industrial applications.[1] For example, ethylene glycol (MEG) is commonly used as a gas hydrate inhibitor, added to water to decrease its melting point; diethylene glycol (DEG) and triethylene glycol (TEG) have long been used as dehydration agents in natural gas streams to prevent corrosion in pipelines. Tetraethylene glycol (TeEG) is a solvent in the purification of aromatic hydrocarbons, while 1,2-propylene glycol (PG) is used in the production of resins.[2] The higher molecular weight polyethylene glycols (PEGs) can be used in the form of aqueous solutions as hydrate inhibitive drilling fluids.[3]

Glymes or glycol ethers, where one (i.e., monoalkyl glymes) or both (i.e., dialkyl glymes) hydroxyl end-groups of a glycol are substituted by an ether group, are known for their great affinity toward acid gases such as CO$_2$ and H$_2$S due to the strong interactions that can be established between the solvent's oxygenated groups and the gas molecules.[4] Hence, a number of studies in the literature report large solubilities of acid gases in glymes or their blends, showing that they are very attractive physical solvents for acid gas removal and other gas processing applications.[5−14] In fact, the UOP Selexol process, which is the state-of-the-art process for high-pressure gas sweetening, uses a blend of polyethylene glycol dimethyl ethers (PEGDME) as a physical solvent (chemical formula: CH$_3$O-(C$_2$H$_4$O)$_n$CH$_3$ where *n* has a specified distribution).[15,16] A low

vapor pressure preventing solvent losses, a good selectivity of H$_2$S over CO$_2$ allowing for the selective absorption of H$_2$S in an absorber and an enhanced recovery of CO$_2$ in the flash drum under a dual stage configuration, low corrosion rates, minimal waste generation, and low energy requirements for solvent regeneration contributed to establish the success of the Selexol process.[17]

On the other hand, alkyl polyoxyethylene glycols also constitute a family of substances that may behave as surfactants (surface active agents) when in aqueous solutions. They are usually represented by their chemical formula H(CH$_2$)$_i$-(OCH$_2$CH$_2$)$_j$OH or simply by C$_i$E$_j$, where *i* refers to the number of CH$_2$ groups in the alkyl residue and *j* refers to the number of EO groups in the molecule that contains one hydroxyl group in one of the chain ends. They can thus be viewed as monoalkyl glymes, where the length of both the alkyl residue and the number of EO repeating units can vary significantly. These nonionic surfactants have numerous applications in areas ranging from cosmetics, detergents, refrigerants, and in EOR, being used in formulations for surfactant flooding.[18−20]

These families of compounds are summarized and sketched in Table 1. Prior to the development or optimization of any new technology involving these compounds, an accurate knowledge of the thermophysical properties and phase behavior of the fluids involved in the process is required for the rigorous design, simulation, and economic evaluation of

Table 1. Families of Compounds Containing EO Groups

Glycols: e.g. triethylene glycol

Mono-alkyl glymes: e.g. diethylene glycol ethyl ether

Di-alkyl glymes: e.g. diethylene glycol dimethyl ether

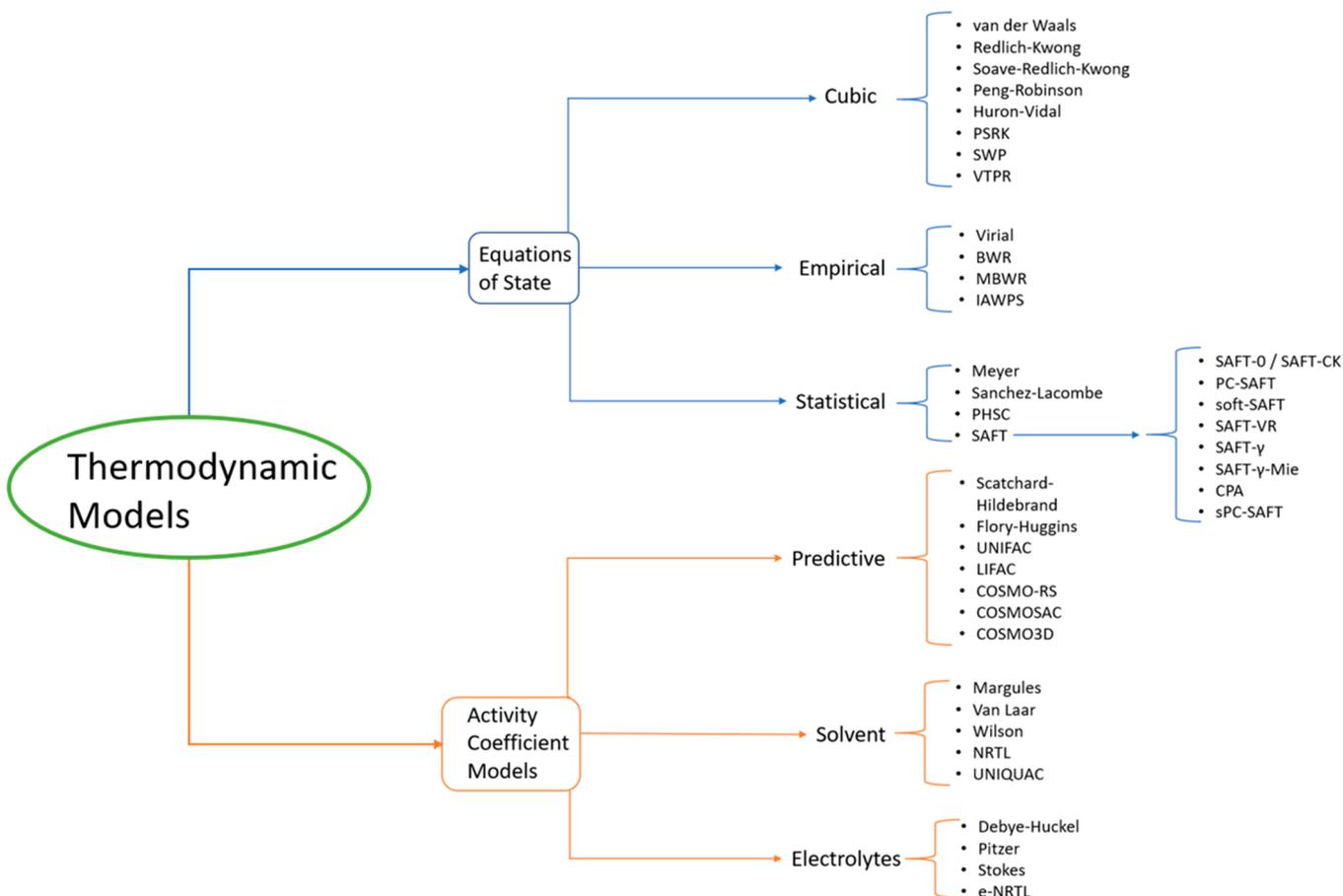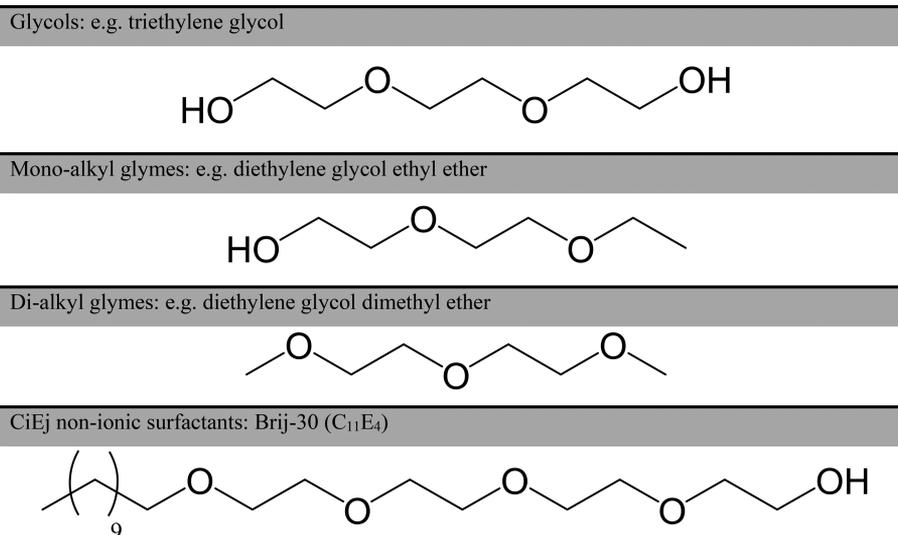| CiEj non-ionic surfactants: Brij-30 ($C_{11}E_4$) |
|---|

Figure 1. A "small" sample of thermodynamic models available in the literature.

the process. Although much data could be obtained experimentally, the cost and time required to perform all the necessary measurements quickly becomes prohibitive, urging the development of thermodynamic models able to describe these type of fluids with ease.

As seen in Figure 1, a large number of thermodynamic models are available with dozens of different activity coefficient models and equations of state (EoSs) reported in the literature,[21] the choice of the most adequate representing a cumbersome challenge for the design engineer not specifically trained in applied thermodynamics. Among these models, advanced molecular-based EoSs, derived from the statistical associating fluid theory (SAFT),[22−24] have found widespread use in academia and a progressive adoption by industry.[25] These models, by being able to explicitly account for strong, short-range, and highly directional forces like hydrogen
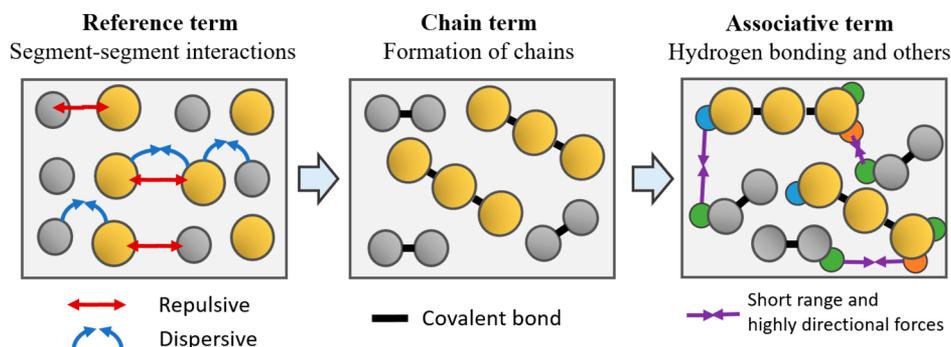
Figure 2. Schematic representation of the physical foundation of SAFT. Yellow and gray colors are used to represent two different segments/components, while green, blue and orange are used to distinguish three different association site types.

bonding, and other complex effects, are potentially more accurate and physically meaningful than the more traditional cubic EoSs or activity coefficient models when applied to the description of a wide range of fluids including water, glycols, and glymes.

In fact, as will be discussed in this work, SAFT-type EoSs have been extensively used to describe compounds containing EO groups. Nonetheless, the modeling approaches considered so far still have known deficiencies that must be highlighted, as they may easily result in a limited applicability, transferability, or accuracy of the different models leading to erroneous results.

Therefore, the aim of this review is to provide an assessment of the modeling approaches, in the framework of association models (e.g., SAFT), used to describe compounds containing EO groups. It intends to outline, both to researchers and industry interested in the modeling of these compounds, what has been achieved for their thermodynamic description. Which SAFT variants have been used? To which systems have they been applied? Which association schemes have been employed? How well do they correlate, extrapolate, or predict experimental data? What else can be explored? These are some of the questions to be addressed throughout this review. The rest of this document is organized as follows: In the next section, a brief introduction to SAFT and its different variants, including the particular case of cubic plus association (CPA) EoS is presented. Then, an analysis and discussion of the literature on the SAFT modeling of glycols, glymes, and C_iE_j surfactants are provided in sections 3−4 before concluding with a general outlook in section 5.

2. SAFT AND CPA: A NEW STANDARD ON THE HORIZON

Despite the simplicity, ease of application, and accuracy of Gibbs excess energy (G^E) models, EoSs have been the industry preferred tool to model phase equilibria and thermophysical properties, mainly due to their ability to provide a global description of the thermodynamic behavior of a fluid (and not just the phase equilibria as occurs with activity coefficient models) and their better performance at high-pressure high-temperature conditions.

Classical EoSs, such as Peng−Robinson (PR) and Soave−Redlich−Kwong (SRK), have been the gold standard in a variety of industrial areas ranging from oil and gas to bulk and specialty chemicals. By combining a mean-field attractive term with a hard-sphere repulsive term, they have several limitations as the hard-sphere reference; although appropriate for small,

simple, and spherical molecules, they exhibit considerable deviations for chainlike fluids. Furthermore, due to their semiempirical character, the physical meaning of the parameters is fuzzy, resulting in poor predictive or extrapolative ability of such equations, requiring large amounts of experimental data for an extensive characterization of a new solvent or fluid mixture.[26]

Moreover, it is undeniable that the systems of interest for industry have become increasingly complex, and cubic EoSs despite being very simple and easy to implement are not able to model molecular-level behavior explicitly, failing when applied to describe associating compounds (e.g., water, glycols, glymes, CiEj surfactants, ionic liquids, amines, ...), making the case for a thermodynamic modeling framework that explicitly considers short-range and highly directional forces (e.g., hydrogen bonding), as well as electrostatic interactions (e.g., Coulombic, dipolar, quadrupolar, etc.).

Clearly, the most apparent progress toward EoSs with such capabilities was achieved by applying statistical mechanics concepts. Wertheim's work on a first order perturbation theory[27−30] and its later implementation in the form of an engineering EoS-SAFT by Chapman and co-workers[22] (original SAFT) and Huang and Radosz[23] (CK-SAFT) represent the major advances toward such an advanced molecular-based EoS.

As shown in Figure 2, in the framework of SAFT, molecules are represented as homonuclear chainlike fluids composed of spherical segments of equal size and energy, exhibiting both dispersive and repulsive interactions, tangentially bonded forming chains that might associate at specific bonding sites present in some of the chain segments (if it is an associating compound). Hence, the system residual Helmholtz energy (A^{res}) is obtained as a sum of different contributions, each of them accounting for a specific effect (eq 1): a segment term (A^{seg}) accounting for the monomer−monomer physical interactions, including both the repulsive and attraction terms; a chain term accounting for the formation of chains from the individual segments (A^{chain}); and an association term (A^{assoc}) that considers strong and highly directional forces such as hydrogen-bonding. (A^{id}) is the ideal term, necessary to determine the total free energy of the system.

$$\frac{A}{Nk_BT} - \frac{A^{id}}{Nk_BT} = \frac{A^{seg}}{Nk_BT} + \frac{A^{chain}}{Nk_BT} + \frac{A^{assoc}}{Nk_BT} + \frac{A^{polar}}{Nk_BT} + ...$$
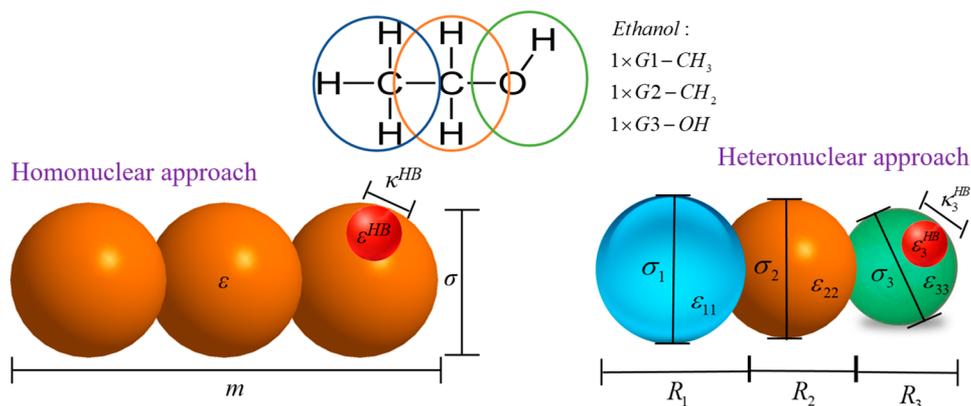
$$(1)$$

Figure 3. Homonuclear and heteronuclear approaches of SAFT-type EoSs illustrated for ethanol.

Wertheim's contributions[27−30] present a theoretically derived model for anisotropic interactions such as hydrogen bonding, in the form of a perturbation term to the Helmholtz free energy of the system as a function of the monomer density, which is related to the so-called association strength.[22] This theory presents the basis for both the chain and association terms of SAFT as the chain term is obtained from the theory in the limit of infinite association by imposing the condition of total bonding between the chain's segments.

By considering different segment terms, mainly in the attractive contribution, several SAFT variants were developed over the years by different research groups. Among the most well-known SAFT-type EoS one could include original SAFT,[22] CK-SAFT,[23] sSAFT,[31] LJ-SAFT,[32] soft-SAFT,[33] SAFT-VR,[34] and PC-SAFT, in both its original[35] and simplified version.[36] More recently, heteronuclear versions of SAFT-type equations (see Figure 3), using a group contribution (GC) approach such as the GC SAFT-VR,[37] SAFT-γ,[38] and SAFT-γ Mie,[39] have also received a great deal of attention. For a detailed description of the different SAFT variants and details about the model equations, the reader is directed to the original publications of the correspondent SAFT version.

An EoS written in terms of the residual Helmholtz energy of the system has the advantage that all the thermodynamic properties can be readily obtained using only derivatives and ideal-gas integrals. Moreover, the theory underlying SAFT makes possible its systematic improvement and extension in a sound manner, allowing the inclusion of additional terms depending on the system's nature such as the addition of a polar term (A^{polar}) to explicitly account for polar interactions. The ease with which SAFT can be coupled to other theories such as the density gradient theory (DGT)[40,41] or free volume theory (FVT)[42] for the calculation of interfacial or transport properties is another key advantage of SAFT-type EoSs.

Furthermore, because of the strong theoretical foundation of SAFT, the model parameters usually have a well-defined physical meaning, allowing for an enhancement of the predictive and extrapolative ability of the models.[43] Most SAFT-type EoS require three pure-component parameters to fully characterize a nonassociating component: the chain length (i.e., the number of segments constituting the chain), m, the segment's diameter, σ, and the segment−segment dispersive energy, ε. If the molecule is self-associating, an association scheme specifying the number and type of association sites, and interactions allowed in the system,

needs to be specified a priori, and the values of association energy ($\varepsilon^{A_iB_i}$ or ε^{HB}) and volume ($K^{A_iB_i}$ or K^{HB}) defined pairwise for each site−site interaction, although, in most cases, the energy and volume of the association sites within a given molecule are considered to be equivalent, resulting in a total of five unknown parameters for a self-associating component such as ethanol illustrated in Figure 3. For a proper definition of an association scheme, Table 7 and 8 of the article by Huang and Radosz[23] present some of the most common association schemes and hence represent a good starting point.

The pure-component parameters of most SAFT models must be regressed from available experimental data, commonly the liquid densities and vapor pressures of the pure compounds in an extensive temperature range. However, the inclusion of additional data such as second-order derivative properties,[44−46] monomer fractions,[47−49] and/or enthalpies of vaporization[25] may improve the model's robustness and accuracy.

If sufficient and reliable pure-component data are not available, alternative approaches need to be considered such as the use of mixture data (as for example, salts[50]) or making use of the parameters transferability (as for example, polymers[43,46,51,52]). The latter is possible because the non-associating parameters of most SAFT variants often exhibit well-defined trends when compared against the molecular weight within a homologous series (see Figure 4 for an example using soft-SAFT), and the association parameters are kept constant within a series of compounds as they are usually
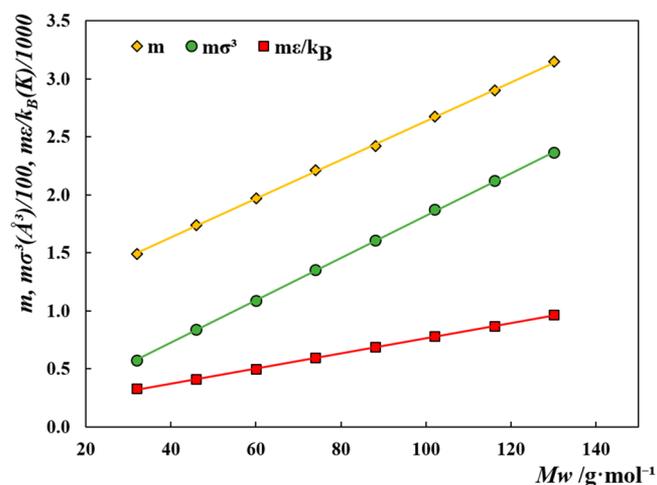

Figure 4. Soft-SAFT parameters for alkan-1-ols reported by Pàmies.[54]

Table 2. Literature Survey on the Modelling of Phase Equilibria of Systems Containing Glycols Using Association Models

glycol component	other components	EoS	assoc. scheme	ref
PEG 200/1500/4000/8000	n-propane/N_2/CO_2	CK-SAFT	2B	Wiesmet et al. (2000)
MEG/TEG/PG	water	CK-SAFT	4C	Li et al. (2003)
TEG	n-hexane/benzene			
MEG	water + methane	CK-SAFT	4C	Li et al. (2006)
TEG	water + methane/ethane/n-propane			
MEG/DEG/TEG/TeEG/PG	n-hexane/n-heptane, methylcyclohexane	CPA	2B/4C	Derawi et al. (2003)
MEG/DEG/TEG	water	CPA	4C	Derawi et al. (2003b)
MEG	water	CPA	4C	Folas et al. (2005)
MEG/DEG/TEG	benzene/toluene	CPA	4C	Folas et al. (2006a)
MEG/DEG	water + benzene			
MEG/TEG	water + toluene			Folas et al. (2006b)
TEG	toluene + n-heptane			
MEG	CO_2/N_2/methane/benzene	soft-SAFT	2B	Pedrosa et al. (2005)
DEG	CO_2			
TEG	n-hexane/benzene			
TeEG	CO_2/benzene			
PEG 200/300/400/600/1000/1500/4000/6000/8000	N_2/CO_2/n-propane/water/methanol	soft-SAFT	2B	Pedrosa et al. (2007)
	ethanol/2-propanol/benzene/toluene			
	ethylbenzene/n-propylbenzene/t-butyl acetate			
MEG	CO_2/N_2/methane/water/n-heptane/PG	sPC-SAFT		Grenner et al. (2007)
DEG	CO_2/water/n-heptane/benzene			
TEG	benzene/toluene/n-hexane/n-heptane/water		4C	
TeEG	benzene/toluene/o-xylene/n-heptane			
PG	water + MEG/n-heptane			
MEG/DEG/TEG/PG	n-heptane	sPC-SAFT	4C	Tsivintzelis et al. (2008)
DEE	water	SAFT-VR	other	Clark et al. (2008)
PEG 2180/3350/5000/8000/21200/1020000				
MEG/TEG/PEG 10^5	water + methane	SAFT-VR	other	Dufal et al. (2012)
TEG	n-Cn (n = 1, 6, ..., 10)/benzene/toluene/water	CPA	4C/6D	Breil et al. (2009)
TeEG	n-heptane		4C/7D	
MEG/DEG/TEG/TeEG	n-alkanes up to C16	CPA	4C/6D/7D	Afzal et al. (2009)
MEG/DEG/TEG	CO_2	CPA	4C	Tsivintzelis et al. (2011)
TEG	methane/CO_2/water	CPA	4C	Kontogeorgis et al. (2011)
MEG	water/n-hexane/2,2,4-trimethylpentane			
MEG/DEG/TEG	CO_2/water/methane	CPA	4C	Tsivintzelis et al. (2016)
MEG/DEG/TEG	CO_2/COS/H_2S	CPA	4C/6D	Afzal et al. (2012)
PEG (different M_w)	water + inorganic acids (ATPS)	ePC-SAFT	4C	Reschke et al. (2014)
MEG	n-hexane/n-heptane/condensates	sPC-SAFT	4C	Liang et al. (2015)
MEG/DEG/TEG/TeEG/PeEG/HeEG/PEG 400		soft-SAFT	D2	Crespo et al. (2017)
MEG/DEG/TEG/TeEG	water	soft-SAFT	D2	Chouireb et al. (2018)
PEG 400/600/1500/6000				
MEG	H_2O/methane/n-hexane/ benzene/toluene	CPA/sPC-SAFT	4C	Liang et al. (2017)
MEG	methane/ethane/n-propane/n-hexane/n-heptane	modified CPA	4C	Palma et al. (2017)
	methylcyclohexane/CO_2/COS/H_2S			
	water/petroleum fluids			
MEG	water/methane/CO_2/H_2S	CPA	4C	Boesen et al. (2017)
MEG	water/methane	CPA-PR	4C	Voutsas et al. (2017)
MEG	water/methane/n-hexane/n-heptane	CPA	3C/4C/4E/4F	Kruger et al. (2018)

capturing the associating role of the same functional groups (e.g., alkan-1-ols family members share the same association parameters). Given the nature of SAFT-type equations, several parameter sets can yield similar results for the pure-component properties. For that reason, selected binary data (normally, liquid–liquid equilibrium (LLE) with an inert compound, e.g.,

n-alkanes) may be used to guide the selection of the best parameter set.[53]

The extension of SAFT and related EoSs to mixtures is usually carried under the van der Waals one-fluid theory using the conventional Lorentz–Berthelot mixing rules to obtain the size and energy parameters between unlike segments. Here, the use of adjustable binary interaction parameters correcting

significant differences in size (η_{ij}/l_{ij}) or energy (ξ_{ij}/k_{ij}) of the molecules are applied when required for an accurate description of the experimental data:

$$\sigma_{ij} = (1 - l_{ij})\frac{\sigma_{ii} + \sigma_{jj}}{2} \text{ or } \sigma_{ij} = \eta_{ij}\frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2}$$

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \text{ or } \varepsilon_{ij} = \xi_{ij}\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{3}$$

From eqs 2−3, η_{ij}/ξ_{ij} are equivalent to $(1 - l_{ij})/(1 - k_{ij})$, commonly used with cubic EoSs. Once these binary interaction parameters are defined for each binary (or set to zero/one in purely predictive calculations), they are used along with the pure-component parameters to perform ternary and multi-component calculations in a predictive manner without any additional fitting or fine-tuning.

When cross-association between different compounds exists, the evaluation of the association term requires the knowledge of the correspondent cross-association energies and volumes which are typically obtained from appropriate combining rules using the self-associating values. Different combining rules have been applied with different association models, but, as they usually lack a physical basis, there is not a universally best choice. As an example, the combining rules employed with soft-SAFT for the interactions between site "A" in component i and site "B" in component j are given below:

$$\varepsilon^{A_iB_j'} = \varepsilon^{B_iA_j'} = \alpha_{ij}^{HB}\sqrt{\varepsilon^{A_iB_i}\varepsilon^{A_j'B_j'}} \tag{4}$$

$$\kappa^{A_iB_j'} = \kappa^{B_iA_j'} = \beta_{ij}^{HB}\left(\frac{\sqrt[3]{\kappa^{A_iB_i}} + \sqrt[3]{\kappa^{A_j'B_j'}}}{2}\right)^3 \tag{5}$$

In eqs 4−5, α_{ij}^{HB} and β_{ij}^{HB} are binary site−site interaction parameters that may be used to correct deviations from the combining rules for the cross-association energy and volume, respectively.

Several extensions, modifications, and improvements of the SAFT approach have been developed over the last few decades. Naturally, an exhaustive description of such modifications is outside the scope of this review, but a number of monographs[26,55] and excellent reviews about SAFT, its capabilities, and applications are available in the literature for further reading.[25,56−63]

One of the most successful modifications of SAFT is the replacement of the segment and chain terms by a cubic EoS (e.g., SRK), leading to "cubic-plus-association" (CPA) EoSs. First proposed by Kontogeorgis et al. in 1996,[64] here denoted as the original CPA EoS, it was later simplified by changing the expression for the radial distribution function, establishing the simplified version of the model (sCPA)[65] that finds widespread use nowadays. For a general overview of the different applications and capabilities of CPA, the reader is directed to the excellent monograph by Kontogeorgis and Folas.[26]

The development of CPA had the purpose of providing a model that was simultaneously based on SRK EoS (widely applied by the petroleum industry) and on the SAFT approach for a correct description of associating fluids. Hence, in the absence of associating components and recalling the additivity present in SAFT approaches (eq 1), CPA reduces to SRK, the EoS with which industry was already familiar, achieving a compromise between accuracy and simplicity, promoting an easier acceptance by industry as the use of a "normal" SAFT-type EoS was often considered unnecessary, except for very specific applications (e.g., polymers).[26]

Like SAFT, CPA requires five pure-component parameters for a self-associating compound but allows for a considerable decrease of complexity and computation time without sacrificing accuracy, making it a very attractive alternative for industry. Both SAFT (normally, the PC-SAFT version of the model) and CPA are already available in many process simulators such as those from AspenTech.

3. MODELING OF GLYCOLS

The first relevant work on the SAFT modeling of glycols appeared 10 years after the advent of SAFT[22,23] when, in 2000, Wiesmet et al.[66] measured the phase equilibria of binary systems composed of PEG (molecular weight in the range 200−8000 g/mol) with either CO_2, n-propane, or nitrogen (N_2). The authors used the CK-SAFT EoS to correlate the experimental data, but, although stating that PEG molecules are able to self-associate via one of the hydroxyl end-groups with either the oxygen atoms in the polymer backbone or the hydroxyl end-group of a neighbor molecule, they only considered the hydrogen bonding character of the hydroxyl end groups. Two association sites were assigned to the PEG molecules following the "2B" scheme suggested for alcohols by Huang and Radosz,[23,24] and the association parameters transferred from ethanol. The PEG nonassociating parameters were regressed from a set of 61 pressure−density−temperature ($p\rho T$) experimental data points in a wide temperature and pressure range for PEG 7500 with a percentage average absolute deviation (%AAD) of 0.1 being reported by the authors. The parameters obtained were kept constant throughout the work for the different PEG molecular weights studied, except for the chain length, which was given in terms of a ratio m/M_w. A binary interaction parameter (BIP), k_{ij}, for each binary system was required in order to achieve a good agreement with the experimental data. These BIPs were fitted to experimental data of the polymer-rich phase, and the authors observed that the k_{ij} parameter was temperature and molecular weight dependent, except for the mixtures with N_2 for which the BIP could be set temperature independent without considerably increasing the deviations. However, for the systems with n-propane and CO_2, linear and quadratic temperature dependencies were necessary, respectively.

Since then, several modeling works using association models to describe the phase equilibria of systems containing glycols have been reported in the literature. The majority of systems investigated in the most relevant works found during our literature survey is outlined in Table 2 along with the EoS and association scheme employed in those studies.

Li et al.[67] also used the CK-SAFT EoS variant to correlate the vapor−liquid equilibrium (VLE) of several binary mixtures containing low molecular weight glycols, namely, EG/TEG/PG + H_2O, EG + PG, TEG + n-hexane/benzene. The "4C" association scheme[23] (two positive and two negative association sites) commonly used for glycols was applied in this work, thus neglecting the possible association through the lone electron pairs on the oxygen atoms of the oxyethylene units. The pure-component parameters for the different glycols were obtained by simultaneously fitting the experimental saturated vapor pressures and saturated liquid densities. For DEG and TEG, given the unavailability of saturated liquid densities, the densities of the saturated vapor phase were considered. One binary parameter, k_{ij}, was required to achieve

a good description of the experimental data. However, for the binary mixtures with water, an additional binary interaction parameter, α_{ij}^{HB}, correcting the cross-association energy was necessary for a quantitative agreement. The model was then applied for the successful prediction of the ternary system H_2O + PG + EG. In a subsequent publication by the same group,[68] the model was applied for the prediction of the thermodynamic inhibiting effect of MEG and TEG. Excellent predictions of the phase equilibria of ternary mixtures MEG + H_2O + methane and TEG + H_2O + methane/ethane/n-propane without additional fitting (i.e., k_{ij} between glycol and n-alkanes equals zero) were given.

Derawi and co-workers[53] applied the CPA EoS, which combines the SRK cubic EoS with the association term from SAFT models, to describe the liquid–liquid equilibrium (LLE) of systems containing glycols (MEG, PG, DEG, TEG, TeEG) and hydrocarbons (n-hexane, n-heptane, and methylcyclohexane), obtaining excellent correlations of the experimental data using a single state-independent BIP. In this work, two possible association schemes ("2B" and "4C") were tested for MEG with the "4C" scheme being shown to be the best choice. The large uncertainties in the experimental VLE data for the pure glycol oligomers were taken into account, and the inclusion of LLE data of binary mixtures with an inert (in this case n-heptane) was suggested in order to guide the selection of the most adequate set of molecular parameters. Otherwise, even the system MEG + n-heptane could not be well reproduced.

In this manner, a final set of parameters for the different glycols ("4C" scheme) was obtained, including glycol + n-heptane LLE data in the experimental data set considered for the fitting. Furthermore, the authors showed that TeEG has a unique behavior if compared to the shorter glycols or PEG 300, translated in a negligible self-association that may be due to the possible folding within itself. A comparison of the infinite dilution activity coefficients (γ^{∞}) of n-heptane in the different glycols was also provided using the BIPs fitted to the LLE data and it showed that CPA performs satisfactorily for these systems, with the highest deviations being observed for MEG.

In a subsequent publication,[69] the model applicability was extended to cross-associating systems by modeling mixtures with water and testing different combining rules for the association parameters. The VLE of binary mixtures MEG/DEG/TEG + H_2O was accurately described, and the CR-1 combining rule was found to be the best overall choice. Two years later, the BIP fitted to the VLE of MEG + H_2O was successfully used to predict the solid–liquid equilibrium (SLE) of this binary mixture, but the ECR combining rule performed better than CR1.[70]

Using the same model and parameters, Folas et al.[71,72] described the VLE and LLE of binary mixtures of MEG/DEG/TEG + benzene/toluene. A new approach to model solvation that consisted of using a cross-association energy taken as half of the association energy of the pure associating compound and a cross-association volume fitted to the binary experimental data was proposed and used throughout this work. Overall, the results obtained highlighted the importance of considering solvation when studying mixtures of non-self-associating aromatics with polar or associating compounds. The results were in general very satisfactory by fitting both the k_{ij} and the cross-association volume between the glycol and the aromatic compound, and, in most cases, the same interaction parameters can be used for both VLE and LLE calculations.

Very good predictions were obtained for the ternary mixtures MEG/DEG + water + benzene, MEG/TEG + water + toluene, and TEG + toluene + n-heptane.

Although promising results were obtained in these works using CPA, the transferability of the molecular parameters to glycols of higher molecular weights was not attempted, nor was the influence of EO groups properly discussed.

Pedrosa et al.[73] modeled four glycol oligomers (MEG, DEG, TEG, and TeEG) using the soft-SAFT EoS. The authors modeled MEG and its oligomers as LJ chains with one associating site at each end group (2B scheme—a two site model) and regressed the correspondent pure-component parameters by fitting to available VLE data (vapor pressures and saturated liquid and vapor densities) of the pure-components, providing an accurate description of the experimental data although no other properties were calculated. The intramolecular interactions were legitimately neglected based on their very low probability due to polymeric steric hindrance and because the existence of ring associating structures cannot be described by TPT1. However, no discussion was presented about the hydrogen bonding character of the inner EO groups and their possibility to act as hydrogen bond acceptors in interactions with neighboring molecules.

The associating parameters ($\varepsilon^{A_i B_i}$ and $K^{A_i B_i}$) were fitted to MEG VLE data, and their values were transferred for the rest of the oligomers. The remaining parameters were found to be correlated to the glycols molecular weight allowing the prediction of parameters for higher chain length members. These molecular models were then used to describe the phase equilibria of different binary mixtures, namely, MEG + CO_2/ N_2/ CH_4/benzene, DEG + CO_2, TEG + n-hexane/benzene, and TeEG + CO_2/benzene. For most of these systems, a state-independent k_{ij} (lower than unity) was required to obtain accurate results, except for MEG + CH_4 and DEG + CO_2 for which the use of a temperature dependent (linear) BIP was necessary to avoid deterioration of the results at high gas concentrations. In mixtures with benzene, the introduction of the polar term removed the need for a BIP, with the model predictions showing an excellent agreement with the experimental phase diagrams.

As illustrated in Figure 5, the majority of publications dealing with the thermodynamic modeling of glycols using association models focused only on the first four members of the series, especially MEG or TEG due to their widespread use as gas hydrate inhibitors and dehydration agents. This is despite the importance of achieving an accurate modeling of higher chain length members that ensure the robustness of the molecular models and parameters proposed and certifies that the physics of the oxyethylene repeating unit is being well captured.

Considering this, in a subsequent study by the same research group,[52] the molecular model developed for EG oligomers by Pedrosa et al.[73] was transferred to PEGs of different molecular weights (200−8000 g/mol) and used to describe the phase equilibria of several mixtures of poly(ethylene glycol) with different types of solvents, including light gases (N_2, CO_2, n-propane), water, alcohols (methanol, ethanol), and aromatics (benzene, toluene, ethylbenzene, and n-propylbenzene).

Again, excellent results were obtained for the mixtures with benzene (with temperature independent k_{ij}), although discrepancies were observed in the mixtures with CO_2 (especially for the lower M_w PEGs) and n-propane as the
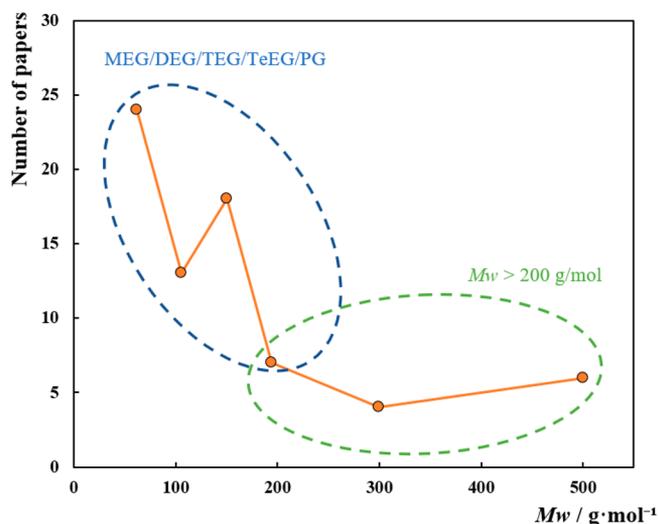
Figure 5. Number of modeling works using SAFT or CPA as a function of the glycol's molecular weight, based on the references presented in Table 2. The points 300 and 500 represent the number of works on the modeling of PEGs with a molecular weight in the range 200−400 g/mol and higher than 400, respectively.

molar fraction of polymer is increased. Satisfactory results were also obtained for the description of the VLE of PEG's with associating solvents such as ethanol, methanol, 2-propanol, and water using one temperature independent k_{ij}. In this work the hydrogen bonding between the polymer ether groups and water was neglected, and, although the VLE seems not to be very sensitive to those association interactions, the effect of water−PEG hydrogen bonding on the LLE of such systems was later shown to be relevant.[74] Furthermore, the authors applied the model to describe the LLE of binary mixtures of PEGs (200−600 g/mol) with aromatic solvents using a BIP marginally dependent on the polymer's molecular weight. Although the model achieved a reasonable description of the upper critical solution temperature (UCST) that characterizes these systems, it was not able to accurately capture the right critical composition. Furthermore, when the model was applied to predict the LLE of PEGs (8000−21000) + *tert*-butyl acetate. which presents both a UCST and a lower critical solution temperature (LCST), only the LCST was reasonably captured by soft-SAFT while it failed at predicting the existence of a UCST.

Grenner et al.[2] applied the simplified version of PC-SAFT to correlate the VLE/LLE of several binary mixtures containing glycols (modeled under the "4C" association scheme): MEG + CO_2/N_2/methane, DEG + CO_2, TEG + benzene/toluene/*n*-hexane, and TeEG + benzene/toluene/*o*-xylene. Overall the performance of sPCSAFT was similar to that of CPA when both are using a temperature-independent BIP.[53,69,71,72] Furthermore, the results obtained for the VLE of mixtures with aromatic hydrocarbons revealed that VLE data could be easily described without explicitly accounting for solvation. This is contrary to the LLE of glycol oligomers with aromatics for which only explicitly accounting for solvation accurate results was obtained. The VLE of binary mixtures of glycol oligomers with water was also investigated, and good results were obtained using a state-independent BIP with deviations lower than those reported by Li and Englezos[67] using SAFT-CK with two adjustable parameters. Also the LLE data for glycols + *n*-heptane reported by Derawi et al.[53] were modeled

using sPC-SAFT, but higher deviations than those reported with CPA were observed, mainly due to the noninclusion of such data in the experimental data set considered for the fitting of sPC-SAFT molecular parameters. Very good predictions without further fitting for the VLE of MEG + PG + water and the LLE of DEG + water + benzene were also presented, with the results for the latter reinforcing the importance of considering the solvation phenomena. In another study, Tsivintzelis et al.[75] compared the performance of sPC-SAFT with the nonrandom hydrogen bonding (NRHB) theory to the modeling of glycol-hydrocarbon LLE, namely, MEG/DEG/TEG/PG + *n*-heptane. Compared to the parameters proposed by Grenner et al.,[2] a different association volume parameter was used for glycols without apparent reason. Both models described in a satisfactory way the LLE data, but in most cases NRHB yielded more accurate correlations than sPC-SAFT, while sPC-SAFT provided the best predictions.

Clark et al.[74] used SAFT-VR (potentials of variable range) EoS to model the closed-loop liquid−liquid immiscibility that characterizes aqueous solutions of PEGs. Contrary to the work of Pedrosa et al.,[52] the hydrogen bonding character of the EO repeating unit was explicitly considered, and the interactions between water and the ether groups of the polymer backbone were taken into account. The authors suggested that for low molecular weight glycols the contribution of the hydroxyl end-groups is the most significant, controlling the miscibility behavior of the polymer, while for higher molecular weight PEGs the miscibility is governed by the EO groups as the effect of the two hydroxyl end groups becomes negligible in comparison to that of the large number of ether units. Hence, a parametrization based on the shorter glycol oligomers (as typically done in the other works) is expected to capture well the contribution of the OH groups while failing to accurately represent the contribution of the EO repeating unit of PEGs, limiting the performance of the equation when using parameters extrapolated from the lighter members for the description of higher molecular weight PEGs.

As no pure-component data are available for polymers due to their immeasurable vapor pressure, the authors opted by characterizing the repeating unit. VLE data of pure diethyl ether (DEE, chemical formula: CH_3-CH_2-O-CH_2-CH_3) was used to obtain the nonassociating parameters that characterize the repeating unit (namely, σ, ε, and λ) considering DEE as a non-self-associating compound. These parameters were later transferred for the modeling of PEG molecules. The chain length parameter, m, for both DEE and PEGs was obtained through an empiric relationship proposed by Jackson and Gubbins.[76]

The unlike association parameters between water and the ether groups were regressed from the LLE data for DEE + water while the values for σ and ε were refined to ensure a good description of the experimental data. However, the cross-association parameters between water and EO groups obtained under this approach could not be used successfully for PEG + water mixtures and had to be simultaneously fitted along with the remaining unlike parameters.

Contrary to DEE, PEG molecules are able to self-associate between the hydrogen and oxygen atoms of the terminal groups (OH−OH bonding) as well as the hydrogen atoms of the hydroxyl groups and the oxygen atoms of the EO repeating units (OH−EO bonding). Hence, three associating site types are assigned: two "e*" sites representing the lone electron pairs on the oxygen atom and one "H*" site representing the

Table 3. Association Schemes Employed in the Modelling of Glycols Using Either SAFT or CPA

Designation	Nº of Association Sites			Schematic Representation
	+	-	+/-	
2B	1	1	-	
4C	2	2	-	
6D	2	4	-	
7D	2	5	-	
D2	-	-	2	
3C	1	1	1	
4E	1	1	2	
4F	-	2	2	

hydrogen atom of each hydroxyl end-group, and two sites "e" to represent the electronegative oxygen atom of each repeating unit. Both "e*−H*" and "H*−e" bonds are allowed in the system. However, for the sake of simplicity and to reduce the number of adjustable parameters, the authors considered all three associating sites to be equivalent (i.e., same association energy and volume). Hence, the self-association parameters between PEG molecules, the cross-association parameters for PEG−water (both for water−OH and for water−EO interactions), and the binary interaction parameter k_{ij} (i.e., a total of seven adjustable parameters) were regressed from the LLE data of aqueous solutions of PEG 2180/8000/21200, providing a very good description of the experimental data with the low critical end points (LCEPs) and upper critical end points (UCEPs) calculated by the model, deviating 5−15 K from the experimental values. Pure predictive calculations were also carried for the aqueous mixtures of PEG 3350/5000/1020000 g/mol.

Overall, a considerable improvement over the results of Pedrosa et al.[52] was achieved, but the large number of parameters fitted to the LLE of the three selected mixtures may mask the real influence of considering the hydrogen bonding character of the EO groups, so further studies would be welcome.

A suitable alternative would be to consider the binary systems EG/DEG + water to obtain the parameters governing the PEG−water interactions through the hydroxyl end-group (water−OH bonding), decreasing the number of parameters to be regressed from PEG aqueous solutions data. This would reinforce the importance of an integrated approach to model similar compounds regardless of their molecular weight or termination (glycols vs glymes).

The molecular model developed in this work was later used by Dufal and co-workers[77] to model the hydrate−dissociation curves for methane and n-propane in EG, TriEG, and a PEG

with a molar mass of 10^5 g/mol and a good qualitative agreement with the experimental data was found.

Breil and Kontogeorgis[78] carried out a thorough investigation of systems containing TEG. Given the availability of new experimental data and the development of new and more elaborate association schemes, a new "6D" association scheme was introduced. In this scheme, and compared to the "4C" association scheme, two additional "negative" association sites were added to represent the lone electron pairs on the two ether oxygen atoms of TEG. This new association scheme is schematically represented in Table 3 which summarizes the different association schemes employed in the modeling of glycols and discussed throughout this work. Despite all sites being considered equivalent in both energy and volume (regardless of mimicking different functional groups), the higher complexity of the association scheme has been shown to be more advantageous than the traditional "4C" scheme improving the description of a number of systems. The new set of parameters for TEG was obtained from fitting to the pure VLE data, LLE data of its binary mixture with n-heptane and VLE data of TEG + methane. The molecular model was then successfully tested for different binary mixtures with n-alkanes (e.g., methane, nC8, nC9, nC10), aromatics (e.g., benzene, toluene) and water in both VLE and LLE calculations and for the prediction of activity coefficients and heat of mixing data. Overall, a good agreement with the experimental data was achieved using a temperature independent k_{ij}, except for the system with water and methane where a linear temperature dependency was required. A similar "7D" scheme (also represented in Table 3) was tested for TeEG, and although more reasonable values for the parameters were obtained (no negligible values for the association parameters were found) the differences in terms of performance were found to be negligible in the description of pure-component data and LLE of the binary mixture with n-heptane. The new "6D" and "7D" models for TEG and TeEG and the "4C" models for MEG and

DEG proposed by Derawi et al.[53] were later used to satisfactorily describe the infinite dilution activity coefficient data of different n-alkanes (up to C16) in these glycol oligomers.[79] Tsivintzelis et al.[80] applied CPA to model glycol + CO_2 binary mixtures using the parameters proposed by Derawi et al.[53] for glycols. Although solvation was found to be crucial in some other systems (e.g., CO_2 + water), when applied to glycol + CO_2 mixtures, calculations were in good agreement with experimental data even when CO_2 was modeled as an inert compound.

To further investigate how accounting for solvation of CO_2 affects the CPA predictions for multicomponent calculations, Kontogeorgis et al.[81] used CPA to model the solubility of CO_2 in TEG aqueous solutions and the phase behavior of the quaternary system water + TEG + methane + CO_2, and again the results were similar to or without explicitly accounting for solvation effects. In this work, the authors also reinforced the good results obtained with CPA when applied to describe glycol + aliphatic hydrocarbon systems by correlating new experimental data for ternary mixtures MEG + water + n-hexane/2,2,4-trimethyl-pentane.

In a later study by the same group,[82] the k_{ij} values between glycols and CO_2 were refitted using not only the liquid phase compositions but also vapor phase data and used to provide reasonable predictions of the solubility of CO_2 in aqueous glycol solutions (MEG/DEG/TEG), the VLE of quaternary mixtures (CO_2 + MEG/TEG + water + methane), and the VLLE of a multicomponent mixture: water + MEG + CO_2 + CH_4 + n-propane + n-hexane.

Afzal et al.[83] reported new experimental data for the solubility of acid gases (COS and H_2S) in glycols and used CPA to correlate the experimental data using the parameters of Derawi et al.[53] for MEG and DEG and those of Breil and Kontogeorgis[78] using the 6D association scheme for TEG. Satisfactory correlations have been achieved using temperature-independent BIPs, but only small improvements were obtained by including solvation or using the more rigorous association schemes.

Reschke et al.[84] applied the electrolyte version of PC-SAFT (ePC-SAFT[85,86]) to model the formation of aqueous two-phase systems (ATPSs) composed of PEGs of different molecular weight and 1 of 16 different inorganic salts as phase forming agents. A new copolymer modeling approach using two types of segments was considered for PEG: end-group segments of type "A" and PEG chain segments of type "B". Only segments of type A carry association sites in order to mimic the hydrogen bonds through the hydroxyl groups following a "4C"-like association scheme.

The dispersive energy of the two segment types differs, but the other parameters (σ and the k_{ij} with other species) are kept the same for both segment types, while the chain length parameter was obtained as a function of the molecular weight (62.068 g/mol for the end-group segments and (M_{PEG}-62.068) g/mol for the chain segments). The parameters for the copolymer approach were fitted to the water activities (VLE data) and densities of PEG (different molecular weights) aqueous solutions between 293 and 333 K simultaneously with a temperature-dependent k_{ij} obtaining parameters similar to those reported by Stoychev et al.[87] using a homopolymer approach to model poly(ethylene oxide) molecules, but lower deviations to the experimental data were achieved. However, the use of one additional parameter in the copolymer approach should be highlighted.

The PEG-pure component parameters fitted in the scope of the copolymer approach were further used to provide reasonable predictions of the cloud points (LLE) of different PEG solutions. The binary interaction parameters between PEG segments and the different ions were fitted directly to the LLE data of ATPSs but found to provide very good predictions for VLE data (water activities), in ternary mixtures PEG + water + salt and their densities at different temperatures. Overall, the study showed that e-PC-SAFT could be an accurate tool to model ATPS related systems, as the %AAD in the concentration of the phase-forming components was only 2.25% with the model showing to be able to predict the influence of PEG's molecular weight, salt, pH, and temperature on the phase separation and the densities of the two-phases. Moreover, specific phenomena like the concentration-dependent phase inversion could be qualitatively predicted by the model. Although excellent indicative results were provided in this study, the assumption made by the authors that "the PEG end-group segments are capable of forming hydrogen bonds, whereas the PEG chain segments are not" has already been shown to be a false assumption when dealing with cross-associating systems either by experiments,[88−94] simulation,[95−97] or theory.[98−102]

Liang et al.[103] regressed new sPC-SAFT parameters for MEG (4C association scheme) considering, in addition to the pure fluid VLE data, the LLE of its binary mixture with n-hexane and n-heptane in the estimation process. The new parameters were then applied to model the LLE of petroleum fluids (three condensates and three oils) + MEG with or without water, achieving a good agreement with the experimental data for the key mutual solubilities on such systems.

In 2017, Crespo et al.[46] provided new experimental data for high-pressure liquid densities of glycol oligomers (from MEG up to HeEG) in wide temperature (283−363 K) and pressure (0.1−95 MPa) ranges. The new experimental data were correlated using the modified Tait-Tammann equation, and the second-order derivative properties isothermal compressibility, k_T, and the isobaric thermal expansivity, α_P, estimated from the equation. Given that the molecular models proposed by Pedrosa et al.[73] for glycol oligomers using soft-SAFT were unable to reproduce the sensitive second-order derivative properties and having available experimental data for more members of the series and in a wide pressure range, a new association scheme ("D2" in Table 3) was proposed in which one associating site of dual nature was assigned per each hydroxyl-end group (two sites in total per glycol molecule). The molecular parameters were then regressed from the pure fluid VLE data (vapor pressures and saturated densities) and two isotherms of the new high-pressure liquid density. For PeEG and HeEG, no VLE data are known, so only the high-pressure liquid densities were considered in the parametrization process. The best and final set of parameters was selected through comparison of the accuracy when used to reproduce the estimated isothermal compressibilities at 323 K. The optimized molecular parameters were found to provide very good descriptions of both VLE and second-order derivative properties and to successfully predict the existence of specific behaviors like the crossover point observed in the α_P data of some glycols. Moreover, and as commonly done with SAFT (recall Figure 4), the parameters were correlated against the molecular weight. These correlations were then used to obtain the parameters for PEG 400 that were then applied to predict

the high-pressure liquid densities of PEG 400 with a %AAD of 0.22. This model for glycols was later applied for the successful modeling of the boiling temperatures (VLE data) of aqueous solutions of glycol oligomers using a temperature-independent BIP.[104] The value of the interaction parameter mediating the water−glycol interactions was found to increase with the glycols molecular weight until an asymptotic value was reached for PEG 400. This asymptotic value was then used to provide an accurate prediction of water activities in PEGs of higher molecular weight (600−6000 g/mol).

Liang et al.[105] recently presented a systematic and fair comparison between CPA and sPC-SAFT performance when applied to the modeling of the fluid-phase equilibria of gas hydrate related systems containing MEG. MEG was modeled using the "4C" association scheme as in the work of Grenner et al.,[2] and the results showed that both thermodynamic models exhibit a similar accuracy.

Palma et al.[106,107] used a modified CPA EoS (here denoted m-CPA) to describe several MEG pure fluid properties including VLE data, liquid heat capacity (C_{p1}) and heat of vaporization (H_{vap}) and the VLE and LLE of several systems containing MEG. The systems investigated include MEG + hydrocarbons (e.g., methane, ethane, n-propane n-hexane, n-heptane, n-nonane, and methylcyclohexane), MEG + acid gases (e.g., CO_2, COS, H_2S), MEG + water, and the MEG + petroleum fluids with and without water previously investigated by Liang et al.[103] Although very good results were obtained considering all gases as nonassociating inert species, 10 different pure-component parameters were necessary to characterize MEG due to the chosen alpha function.

Boesen et al.[108] compared the SRK with the Huron-Vidal advanced mixing rules[109] and CPA for systems composed of MEG, water, and gases (CH_4, CO_2, and H_2S). The model and parameters for MEG proposed by Derawi et al.[53] were used in CPA, and overall, similar results were obtained for both models except for the MEG content in the gas phase of mixtures rich in CO_2 for which additional experimental data are required for a better comparison of the models performance.

Voutsas et al.[110] applied a different version of CPA (CPA-PR) to model the phase equilibrium of different binary and ternary mixtures involving MEG, modeled using a "4C" association scheme, water, and methane, and naturally a significant improvement over the PR EoS was observed, especially in the ternary mixture.

Very recently Kruger et al.[111] implemented binary association sites (able to interact with both positive or negative sites) in the modeling of MEG by proposing three new association schemes ("3C", "4E", and "4F", see Table 3). These three association schemes, and an improved parameter set for the literature "4C" scheme, were tested against different data types. The results showed that "4E" and "4F" were virtually indistinguishable in terms of performance, and while each new set of parameters showed an improvement over the literature parameters, no association scheme was universally the best choice. The same research group has been actively extending the experimental data available for natural gas and MEG related systems. An example is the difficult VLE measurements carried for the ternary system MEG + water + methane and for a 20-component mixture (MEG + water + natural gas). Both sets of experimental data were satisfactorily modeled with CPA using the available molecular models and parameters.[112,113]

An analysis of the references contained in Table 2 shows that different association models have been used for the thermodynamic modeling of glycols. However, as shown in Figure 6, more than half of the works published in this topic
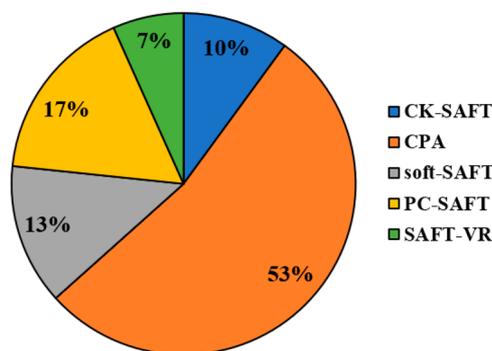

Figure 6. Percentage of publications using different association models for the modeling of systems containing glycols.

were carried out using the CPA EoS, in part thanks to the extensive work of Kontogeorgis and co-workers[25,26,81] that have shown a long-term interest in gas-hydrate related systems.

Nonetheless, most of their works deal only with MEG, DEG, and TEG, and an evaluation of the performance of CPA when used to describe larger PEG molecules is still missing, probably due to the poorer transferability of CPA parameters when compared to other SAFT-type EoSs. Similar works doing the opposite (only modeling larger PEG molecules) are also common in the literature such as those of Wiesmet et al.[66] or Reschke et al.[84]

The works of Pedrosa et al.[52,73] and Crespo et al.,[46,104] although providing such transferability assessments, have also shown some deficiencies as both have built their models parametrization solely around the shorter oligomers. This is expected to fail on correctly capturing the effect of the oxyethylene repeating unit as the effect of the hydroxyl end-groups is still the most relevant. This seems to result in somehow inaccurate results, especially when the model is used to describe the LLE of PEG-containing systems as shown by Pedrosa et al.[52] In the work of Crespo et al.[46,104] no LLE results were provided at all to corroborate this theory. Hence, more works on a transversal modeling of glycols would provide important information considering the applicability limits of the different models and enable a fair comparison of the different association models while contributing to a better description of the effect of M_w in the thermophysical properties of pure glycols and glycol containing systems.

Another major issue, common to most works highlighted in Table 2, is that only the hydrogen bonding character of the hydroxyl end groups is explicitly accounted through the increase of the number of association sites. Hence, as shown in Figure 7, the "4C" association scheme ends up being the most used to describe glycols. Very few works have used association schemes of higher complexity to describe MEG/TEG/TeEG[78,111] or PEGs[74] in the framework of association models. The promising results obtained in these studies suggest that the use of additional association sites to explicitly account for the hydrogen-bond acceptor character of the lone electron pairs on the oxygen atoms of the EO groups, especially as a function of the number of EO groups, should be better investigated, decreasing the gap shown in Figure 7, while
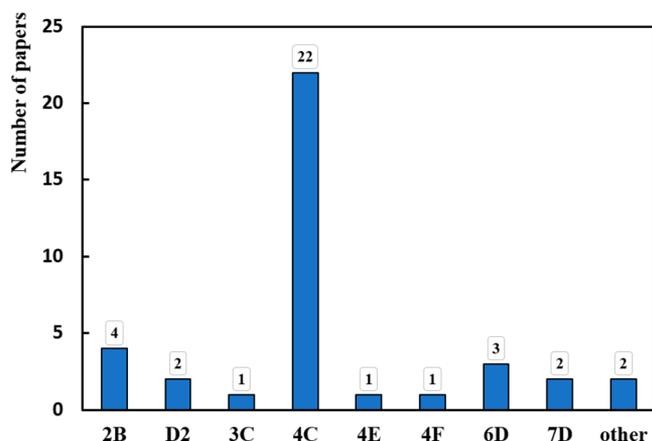
Figure 7. Association schemes (Table 3) used to describe the hydrogen-bonding character of glycols in the framework of association models.

allowing for a more careful analysis of the relation performance/computational cost of different association schemes. The use of binary association sites to describe the hydroxyl group instead of two sites to describe the hydroxyl end groups can also be investigated.

Throughout this chapter, qualitative comparisons of the different models and approaches were made whenever appropriate, although quantitative analysis would have been preferred. Unfortunately, such analyses are difficult because of the different types and sources of experimental data used in the parametrization procedure, the different binary and ternary systems studied, and experimental data sources used by the authors, resulting in different (T, p, x) conditions, and mainly because in most works deviations from experimental data are not given explicitly. When deviations from experimental data are presented (e.g., in tabular form), different metrics (see eqs 6−7) are used such as the root-mean-square deviation (RMSD) or the average absolute deviation (AAD). Therefore, such quantitative analysis can lead to erroneous and unfair conclusions and should be considered with caution.

An attempt at carrying such an analysis is presented in Table 4 where for some of the more common binary mixtures containing MEG and TEG, the deviations from the experimental data obtained using different approaches are summarized.

$$ \text{RMSD} = \sqrt{\sum_{i=1}^{N} \left(\frac{x_i^{\text{calc}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right)^2 / N - 1} \qquad (6) $$

$$ \text{AAD} = \frac{1}{N} \sum_{i=1}^{N} \frac{|x_i^{\text{calc}} - x_i^{\text{exp}}|}{x_i^{\text{exp}}} \qquad (7) $$

As observed in Table 4, for the system MEG + water, MEG + n-hexane, or TEG + n-hexane, deviations to the experimental pressure are very similar regardless of the association model used. Most SAFT-variants are expected to have similar accuracies when used to describe most systems, provided the compounds are modeled using the same association schemes, using the same number of binary interaction parameters and following similar approaches in the parametrization procedure.

On the other hand, the work of Breil et al.[78] shows that the use of different association schemes to model TEG may have an impact on the performance of the model when used to

describe the phase equilibria of mixtures. Considering the results presented in Table 4, the "6D" association scheme proposed by Breil et al.[78] performs slightly better than the "4C" scheme in the modeling of LLE of TEG + n-heptane/benzene, while the latter performs better when applied to the VLE of TEG + water. This reinforces the need for systematic studies on the advantages of using more realistic association schemes.

Boesen et al.[108] presented a comparison between CPA and SRK-HV when used to model MEG-related systems such as MEG + CO$_2$, and both models showed similar deviations (~8% AAD in the gas concentration in the liquid phase) that compare well with the results reported by other works such as Palma et al.[106] It is our opinion that cubic EoS coupled with the Huron-Vidal mixing rules[109] should be considered as benchmark models, and the performance of association models and its different approaches should be more often compared with these types of models in order to assess the real need for complex association models like SAFT. Further studies are required as results were only presented for systems with MEG, which is the shortest glycol oligomer, and do not present the inner oxygen atoms whose influence needs to be properly captured by models. Moreover, one of the strengths of SAFT-type models may be related to the higher transferability of its parameters, and not with its accuracy in describing a particular system.

Also, the type of experimental data used to regress the pure-component parameters has an impact on the performance of the model when applied to mixtures. An example is the better performance of CPA in the work of Afzal et al.[83] when compared to Tsivintzelis et al.[82] as the parameters used in the former work were regressed from VLE of TEG + methane in addition to the pure fluid VLE data and LLE of its mixture with n-heptane as considered in Tsivintzelis et al.[82]

4. MODELING GLYCOL ETHERS - GLYMES AND CiEj NONIONIC SURFACTANTS

When compared with glycols, studies involving the application of SAFT-type EoSs to the thermodynamic modeling of glycol ethers are much scarcer. The most relevant works on the modeling of glycol ethers using association models are summarized in Table 5 and will be discussed in this section.

Some of these works relate to the thermodynamic modeling of glymes, a term that, in this paper, is used to define glycol ethers used as physical solvents, e.g., in the removal of acid gases from natural gas streams. Others comprise the study of glycol ethers with a surface activity, commonly known as C$_i$E$_j$ nonionic surfactants.

For glycol dialkyl ethers (here denoted as dialkyl glymes), only three works by Kiesow et al.,[114] Nannan et al.,[115] and Polishuk and Yitzhak[116] were found in the literature prior to 2018, and they all share one crude assumption: the dialkyl glymes are modeled as nonassociating species, neglecting the hydrogen bonding character of the inner EO groups that are able to cross-associate with other species.

Therefore, the difference between an n-alkane and a glycol ether is, in these works, exclusively accounted for by the specific values of the pure-component parameters as no association sites are added into the core of the molecules and the association term is disabled. If this is perfectly reasonable in the works of Nannan et al.,[115] and Polishuk and Yitzhak,[116] it does not hold in the work of Kiesow et al.,[114] where binary mixtures with self-associating compounds (e.g., 2-propanol) were investigated.

Table 4. Deviations from Experimental Data in the Modelling of VLE and LLE of Binary Systems Containing MEG and TEG[a]

System A: MEG (1) + Water (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	Δy	Δp (%)	ref
VLE	371.15−383.15	2	CK-SAFT	4C	4	0.0157[b]	4.9[b]	Li et al. (2003)
VLE	343.15/363.15	1	sPC-SAFT	4C	4	0.00345	3.0	Grenner et al. (2007)
VLE	343.15/363.15	1	sPC-SAFT	4C	4		2.5	Liang et al. (2017)
VLE	343.15/363.15	1	CPA	4C	4		2.8	Liang et al. (2017)
VLE	298.03	1	CPA-PR	4C	4		2.4	Voutsas et al. (2017)
VLE	343.15/363.15	1	m-CPA	4C	4		3.2	Palma et al. (2017)

System B: MEG (1) + CO_2 (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	$\Delta x CO_2$	Δp (%)	ref
VLE	323/373/398	1	sPC-SAFT	4C	4		26.0	Grenner et al. (2007)
VLE	288.15−423.15	1	CPA	4C	4	~8		Boesen et al. (2017)
VLE	323/373/398	1	m-CPA	4C	4	9.6		Palma et al. (2017)

System C: TEG (1) + Water (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	Δy	Δp (%)	ref
VLE	477.59 K	2	CK-SAFT	4C	4	0.0375[b]	2.32[b]	Li et al. (2003)
VLE	297.60/332.60 K	1	sPC-SAFT	4C	4		8.6	Grenner et al. (2007)
VLE	297.60/332.60 K	2	CPA	4C	4		4.7	Derawi et al. (2003)
VLE	332.60 K	2	CPA	4C	4		3.5	Breil et al. (2009)
VLE	332.60 K	2	CPA	6D	6		11.3	Breil et al. (2009)

System D: TEG (1) + CO_2 (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	$\Delta x CO_2$	Δp (%)	ref
VLE	298.15−398.15 K	1	CPA	4C	4		4.1	Tsivintzelis et al. (2011)
VLE	298.15−398.15 K	1	CPA	4C	4	2.4		Afzal et al. (2012)
VLE	298.15−398.15 K	1	CPA	4C	4	5.3		Tsivintzelis et al. (2016)

System E: TEG (1) + n-hexane (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	Δy	Δp (%)	ref
VLE	473	1	CK-SAFT	4C	4	0.0235[b]	7.89[b]	Li et al. (2003)
VLE	473	1	sPC-SAFT	4C	4	0.0225	9.07	Grenner et al. (2007)

System F: MEG (1) + n-hexane (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	$\Delta x2$ in (I)	$\Delta x1$ in (II)	ref
LLE	307.95−330.35	1	CPA	4C	4	5.9	11.00	Liang et al. (2017)
LLE	307.95−330.35	1	sPC-SFT	4C	4	3.7	4.20	Liang et al. (2017)
LLE	307.95−330.35	*	m-CPA	4C	4	41.45	15.95	Palma et al. (2017)

System G: MEG (1) + n-heptane (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	$\Delta x2$ in (I)	$\Delta x1$ in (II)	ref
LLE	316−352	1	sPC-SAFT	4C	4	16.9	20.30	Grenner et al. (2007)
LLE	316−352	*	m-CPA	4C	4	38.3	16.02	Palma et al. (2017)

System H: TEG (1) + n-heptane (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	$\Delta x2$ in (I)	$\Delta x1$ in (II)	ref
LLE	309−410	1	sPC-SAFT	4C	4	29.1	39.20	Grenner et al. (2007)
LLE	310−350	1	CPA	4C	4	4.6		Derawi et al. (2003)
LLE	310−350	1	CPA	4C	4	9.7		Breil et al. (2009)
LLE	310−350	1	CPA	6D	6	3.8		Breil et al. (2009)

System I: TEG (1) + benzene (2)

PE	T-range (K)	no. BIPs	model	AS	NSites	$\Delta x2$ in (I)	$\Delta x1$ in (II)	ref
LLE	278−288	1	sPC-SAFT	4C	4	30.5	8	Grenner et al. (2007)
LLE	278−288	2	CPA	4C	4	0.9	16.3	Folas et al. (2006)
LLE	278−288	2	CPA	6D	6	4.8		Breil et al. (2009)

[a]All deviations are expressed in %AAD except where otherwise indicated. [b]Deviations expressed in RMSD.

Nonetheless, even in the other two works where only pure-component properties or the study of their blends was considered, a further transferability of the molecular models developed solely using pure fluid data as in the work of Nannan et al.[115] may be compromised, and inaccurate results may be obtained when modeling mixtures.

Kiesow et al.[114] applied the PC-SAFT EoS to study the oiling-out effect of blends of polyethylene glycol dimethyl ethers (PEGDME X where X is the mean molecular weight of the solvent). This solvent is similar to that used in the Selexol process (chemical formula: $CH_3O[CH_2CH_2O]_nCH_3$, where n has a specific distribution). The phase equilibria of two different blends in different solvents was investigated, namely,

Table 5. Literature Survey on the Thermodynamic Modelling of Glycol Ethers Using Associative EoS

glycol ether	other components	EoS	assoc. scheme	ref
PEGDME 1000/2000	diethylketone/ethyl acetate/2-propanol	PC-SAFT		Kiesow et al. (2010)
EGDME/DEGDME/TriEGDME/TeEGDME		PC-SAFT		Nannan et al. (2013)
PeEGDME/HeEGDME/HeptEGDME/OctEGDME/ NonEGDME				
TriEGDME		SAFT + cubic		Polishuk and Yitzhak (2014)
EGEE/DEGEE/DEGDEE/DEGDME		soft-SAFT	D1/−	Navarro et al. (2017)
TriEGDME/TeEGDME/DEGME/TeEGME				
DEGME/DEGEE/DEGDME/DEGDEE	CO_2	soft-SAFT	D1/−	Amaral et al. (2018)
CnE6/CnE8/CnE9	water	segment-based SAFT		Li et al. (1998)
C10En/C12En				
C4E1/C10E5	water	SAFT-HS	N3	Garcia-Lisbona et al. (1998)
several CiEj surfactants	water	SAFT-HS	N3	Garcia-Lisbona et al. (1998b)
C1E1/C2E1/C4E1/C4E3	methanol/ethanol/propanol/MEG/ water	CPA	2B/3B	Garrido et al. (2008)
	hexene/octane/toluene/benzene/ethyl acetate			
PEO/PPO/Pluronics	CO_2	PC-SAFT	2B	Stoychev et al. (2009)
C1E1/C2E1/C4E1	hexane/octane/dodecane/water/ propanol	sPC-SAFT	3B	Avlund et al. (2012)

Table 6. Association Schemes Employed in the Modelling of Glycol Ethers Using Association EoSs

PEGDME 2000 and PEGDME 1000 in diethylketone, ethyl acetate, and 2-propanol. The PEGDME blends were modeled under a pseudo-pure-component approach as a nonassociating compound and their molecular parameters (m as a function of Mw) regressed along with the BIP from the solubility data of PEGDME 2000 + diethylketone. The binary interaction parameters of PEGDME/ethyl acetate and PEGDME/2-propanol were then fitted to the solubility data of the binary mixtures with PEGDME 2000. Afterward, the parameters were transferred to PEGDME 1000 and used to satisfactorily predict their solubility in the different solvents.

Nannan et al.[115] also applied PC-SAFT to the modeling of PEGDME solvents. Again, the glymes were considered as nonassociating species despite the presence of the ether oxygens. The pure-component parameters were individually regressed from pure VLE data for the first four members ($n = 1, ..., 4$) of the dialkyl glymes family, namely, ethylene glycol dimethyl ether (EGDME), diethylene glycol dimethyl ether (DEGDME), triethylene glycol dimethyl ether (TriEGDME), and tetraethylene glycol dimethyl ether (TeEGDME). The sets of parameters obtained were then used to develop correlations

for the pure-component parameters against the glymes' molecular weight. These correlations were further used to obtain the pure-component parameters for glymes with $n = 5−9$. PC-SAFT was then used to predict the Selexol solvent liquid density, and heat capacity using an approximate composition, showing a reasonable agreement with the experimental data.

Polishuk and Yitzhak[116] applied the FVT and the modified Yarraton-Satyro correlation coupled to the SAFT + cubic EoS[117] to successfully model the viscosities of different compounds including TriEGDME. The EoS parameters proposed for this compound were shown to be able to accurately describe its liquid density, speed of sound, and isothermal compressibility, but results for the vapor pressure were not shown. The simultaneous accurate description of both densities and derivative properties may however be attributed to the higher number of parameters required by this EoS, where five parameters are used to describe a non-associating molecule.

More recently, in our group, the molecular model previously proposed for glycols in the framework of soft-SAFT EoS[46] was extended to the thermodynamic modeling of both mono- and

dialkyl glymes.[43] Following our previous work, only the hydroxyl end-groups were considered to hydrogen bond, and thus, a binary association site is assigned per each hydroxyl group ("D1" association scheme in Table 6). Consequently, the dialkyl ethers studied were also modeled as nonassociating species as in the previous works. The molecular parameters for each glyme were regressed from pure fluid VLE data, one single isotherm of the experimental $p\rho T$ data, and isothermal compressibilities (both at 323 K) experimentally measured in the same work. Results similar to those previously reported for glycols[46] were obtained, and the parameters were again successfully correlated against the molecular weight in two different series: one for mono- and another for dialkyl glymes (the presence of the association term induces significant changes in the parameter values[43]). The molecular parameters obtained for glymes were further analyzed through comparison with the soft-SAFT pure-component parameters reported for n-alkanes,[118] alkan-1-ols,[119] and glycols,[46] exhibiting the expected trends, supporting the robustness and transferability of the proposed models. The transferable molecular parameters were then used for the successful prediction of the atmospheric pressure densities of PEGDME 250 modeled as a pseudopure component. In a later work,[14] this molecular model was used to accurately describe the CO_2 solubility in four glymes (two mono- and two dialkyl glymes). However, to achieve a quantitative description of the experimental data in the whole temperature and pressure ranges, both size (η_{ij}) and energy (ξ_{ij}) related BIPs were necessary. Still, both parameters were found to be state-independent, and the former was kept constant for all the systems investigated.

For C_iE_j surfactants, a larger number of studies can be found, and they are not exclusively related to phase equilibria modeling. Li et al.[120] used the segment-based UNIversal QUAsiChemical activity coefficient model (s-UNIQUAC) and a segment-based SAFT based on the original SAFT[22] to calculate the activity coefficients of surfactant molecules in water and correlate the critical micellar concentration (CMC) of single aqueous surfactant systems with a series of alkyl polyoxyethylene glycols (C_iE_j) nonionic surfactants being investigated. Two types of segments were used to describe a C_iE_j molecule: one describing the methylene groups and the other representing the EO repeating unit (C_2H_4O). The size and energy parameters for the two types of segments were simultaneously fitted to experimental CMC data of aqueous solutions of a few C_nE_8 surfactants at 25 °C (%AAD = 9), with the segment diameter being described as a function of the number of segments in the molecule resulting in a total of three adjustable parameters for each type of segment. The SAFT association term was neglected in this work, although a dipole term was used to describe the water dipole.

These parameters were later used to predict the CMC at 25 °C for C_nE_6, C_nE_9, $C_{10}E_n$, and $C_{12}E_n$ series, with SAFT exhibiting a very good agreement with the experimental data (%AAD ranging between 8 and 14%) and a better performance than s-UNIQUAC or Chen-NRTL models. This work was later extended by the same group to describe ionic surfactants by incorporating the mean spherical approximation (MSA) within their approach.[121]

Nieves Garcia-Lisbona et al.[122] used the SAFT-HS[76] (hard-spheres) to describe the phase equilibria of binary aqueous solutions of C_4E_1 and $C_{10}E_5$. The C_iE_j molecules were described as associating chains containing three associating sites to represent the hydroxyl end group: one negative site,

"e", one positive site, "H", and an additional negative site, "e*", with the latter being only able to establish cross-interactions with water; i.e., "e–H" interactions are allowed, but "e*–H" are not. Three negative association sites, "O" per EO repeating unit, are used to mimic the cross-interactions between water and the ether oxygen atoms, while "O–H" self-interactions are forbidden. According to the authors "the steric hindrance of the molecule is too large for C4E1-C4E1 hydrogen bonding interactions to occur favorably through the ether oxygen down the chain". This association scheme is schematically represented in Table 6.

The number of sites chosen to represent the EO repeating unit (three "O" sites) was chosen arbitrarily to obtain the best agreement with the experimental data rather than following any logical or theoretical basis for which two sites would have seemed more obvious (i.e., one per each lone electron pair).

The nonassociating parameters (σ and ε) were transferred from n-alkanes, while the self-association parameters were fitted to the vapor pressures of C_4E_1. The number of segments is the only parameter accounting for the differences between pure C_iE_j molecules and was obtained from the following empirical relation:

$$m = \frac{C + O - 1}{3} + 1 + 0.2 \tag{8}$$

where C and O represents the contribution due to the number of methylene groups and ether oxygen atoms that contribute equally to the number of segments and 0.2 accounts for the terminal hydroxyl group.

Concerning the unlike interactions between water and C_iE_j molecules, the cross-association energy between the hydroxyl end-group and water was transferred from the system 1-butanol + water, and the cross-association energy for interactions through the oxygen ether atoms was fitted to the experimental LLE data of C_4E_1 and transferred for the modeling of $C_{10}E_5$. However, the unlike dispersive energies, ε_{12}, were different in each system. On the other hand, the cross-association volumes were successfully obtained through appropriate combining rules without additional fitting.

Following this approach, the formation of a closed loop immiscibility region was adequately captured by the model that also allowed for reasonable predictions of the phase behavior at conditions different than those considered in the optimization procedure. Despite the reasonable results, the authors suggested that the use of a more sophisticated version of SAFT would probably yield better results.

In a subsequent publication by the same authors,[18] the study was extended to the aqueous solutions of a wide range of alkyl polyoxyethylene ethers, assessing the model parameters transferability to different C_iE_j surfactants through an examination of their cloud curves. Although the general trends could be reproduced using transferable parameters, the unlike dispersive energies, ε_{12}, were again fitted individually to the LCST of the liquid–liquid phase equilibria of each system. Nevertheless, a quadratic dependence of ε_{12} on the number of ethoxy groups (j) and a linear dependence on the number of methylene groups on the hydrophobic tail (i) were found. The results showed that under this approach, SAFT-HS could describe the cloud curves of several surfactants that exhibit both an LCST and UCST, with the critical temperatures and extent of immiscibility being in good agreement with the experimental data.

Furthermore, the relationship between ε_{12} and the values of i and j was used to predict the orthobaric LLE of aqueous solutions of other 140 members of the C_iE_j family. Although there were some significant discrepancies with experiments in whether a closed loop behavior is found, when an LCST is predicted and the value can be compared with experiments, a maximum discrepancy of 31 K was observed, with deviations as low as 1 K being reported for some systems.

Herdes et al.[123] used the soft-SAFT EoS to predict the phase equilibria and aggregate formation as a function of pressure for simple general surfactant molecules, analyzing the effect of the position and number of association sites on the molecular models considered for the surfactant molecules. The good agreement obtained with Monte Carlo (MC) simulations revealed that the theory can qualitatively capture the aggregate formation and fraction of unbounded molecules for specific locations of the association sites, allowing for the investigation of the aggregate formation of real surfactant molecules along with their thermodynamic properties and phase equilibria. However, no further studies on this matter have been reported.

Garrido et al.[124] used the CPA EoS to model the VLE and LLE of several binary mixtures of glycol ethers, namely, C_1E_1, C_2E_1, C_4E_1, and C_4E_3 with aliphatic and aromatic hydrocarbons (e.g., *n*-hexane, *n*-octane, toluene, benzene), polar (e.g., ethyl acetate), and associating compounds (e.g., methanol, ethanol, propanol, MEG, and water). The 2B and 3B association schemes (see Table 6) were considered for the glycol ethers, and both schemes consider only the effect of the hydroxyl groups without an explicit treatment for the ether oxygens. For cross-associating mixtures, two different combining rules were applied and compared, but none of the association schemes or combining rules were universally the best option, although for the LLE of aqueous mixtures, the more complex 3B association scheme often yielded slightly better results.

Concerning VLE results, good correlations were obtained for all mixtures, except for those with water for which a temperature-dependent BIP was required. Concerning the LLE, the model failed to accurately describe the system C_4E_1 + water and the LLE of glycol ethers + *n*-alkanes for which only a qualitative correlation was provided. Further improvements on the description of the LLE mixtures with *n*-alkanes were achieved when the covolume parameter of CPA was obtained from a correlation as a function of the van der Waals volume developed using the covolume parameters of several compounds of different families (see Figure 7 of Garrido et al.[124]). CPA was also used to predict the second virial coefficients of different glycol ethers, but good agreement with the experimental data was only obtained when using the final refined parameters. Moreover, the erratic behavior displayed by SRK at low temperatures was not exhibited by CPA even when using the parameters without the fixed covolume.

Stoychev et al.[87] applied PC-SAFT to study the phase behavior of commercially available poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) block copolymers (PEO−PPO-PEO), also known as Pluronics L, in compressed CO_2. Again, only the hydrogen bonding character of the hydroxyl groups was considered by assigning one proton donor site "A" and one proton acceptor site "B" to each hydroxyl end-group. The pure-component parameters (m being obtained as an m/M_w ratio) for each homopolymer (poly(ethylene oxide), PEO, and polypropylene oxide, PPO), and the BIPs mediating "PEO−CO_2" and "PPO−CO_2"

interactions were regressed from pure liquid density data and selected phase equilibria data of binary mixtures of a hydroxyl terminated PEO and PPO homopolymers (with M_w of 600 and 2000/4000 g/mol, respectively) with CO_2. To describe the Pluronics copolymers, the two pure-component association parameters for PPO were not considered as both OH groups were replaced by two PEO blocks. Following this approach, PC-SAFT was able to correlate the experimental data for Pluronics L as a function of concentration, molar mass, and copolymer composition. However, the binary interaction parameters mediating the unlike dispersive energies between "PEO−CO_2" and "PPO−CO_2" could not be successfully transferred for the modeling of Pluronics R, i.e. PPO−PEO-PPO copolymers.

Avlund et al.[125] applied the sPC-SAFT, with and without the inclusion of a new theory for intramolecular association, to the modeling of binary mixtures containing glycol ethers (C_1E_1, C_2E_1, and C_4E_1). Glycol ethers were modeled using a "3B" association scheme with one proton donor site and one proton acceptor site for the hydroxyl end group and one proton acceptor site for the ether oxygen. Two different sets of molecular parameters were obtained for each glycol ether, with and without explicitly accounting for intramolecular association, by regression of the experimental pure fluid VLE data. The results obtained in the modeling of self-associating mixtures (i.e., mixtures of glycol ethers with an inert compound) show that as previously observed by Garrido et al.[124] with CPA both models failed to correctly correlate the LLE of glycol ethers + *n*-alkanes underpredicting the immiscibility area. Nonetheless, when the BIP is fitted to match the UCST, sPC-SAFT with intramolecular association deviates similarly in the two phases, while the LLE calculated without intramolecular association is shifted toward lower glycol ether contents.

VLE and LLE results for some cross-associating mixtures were also presented in this work, demonstrating the better performance of sPC-SAFT when intramolecular association is explicitly accounted, suggesting that the inner EO groups play indeed a significant role in the phase behavior of glycol ether-containing systems. However, in the case of binary mixtures with water, neither of the two approaches was able to correlate the closed-loop behavior, significantly overestimating the immiscibility area both in temperature and composition, providing worse results than those obtained with CPA.[124] Finally, the influence of pressure on the LLE of glycol ethers + water was also investigated with the inclusion of intramolecular association resulting in a better prediction of the pressure effect.

A quick analysis of Table 5 shows that due to the different applications known to glycol ethers, a more uniform distribution of the number of publications per association model is observed as shown in Figure 8. Contrarily to glycols, CPA is no longer the dominant association model, with PC-SAFT being the most used model in the literature.

On the other hand, the association schemes employed in the different studies, except for the elegant work of Garcia-Lisbona et al.,[18,122] do not account explicitly for the hydrogen bonding character of the oxyethylene units, and, consequently, the role of EO groups in the surfactant-like behavior exhibited by glycol ethers is still far from being well understood, and additional studies are required.

Moreover, except for the work of Crespo et al.,[43,46] who presented a systematic analysis of the soft-SAFT pure-
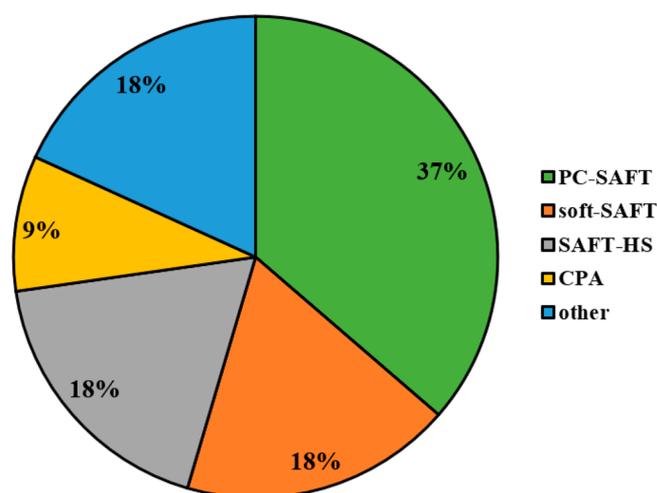
Figure 8. Association models used in the thermodynamic modeling of glycol ethers.

component parameters for different families of compounds, aiming at better understanding how the addition of different functional groups is reflected in the values of the molecular parameters, no similar approach has yet been carried between glycols and glycol ethers despite being constituted by the same functional groups. Hence, the molecular models developed for glycols and glycol ethers are frequently developed independently, although important information, and a sounder parametrization, could be obtained by a more comprehensive approach.

5. PERSPECTIVES AND CONCLUDING REMARKS

As illustrated in the previous sections, the thermodynamic approaches currently used to model systems containing glycols, and glycol ethers have known limitations due to some simplifications imposed on the model parametrization. Such drawbacks must be addressed if one aims at the improvement of the performance, extrapolative, and predictive ability of the existing thermodynamic models.

First and foremost, most works discussed (with very few exception, e.g., Reschke et al.[84]) use homonuclear versions of SAFT-type EoSs (the most common), which treats molecules as homosegmented chains composed of equal-sized spherical segments tangentially bonded to each other. With this approach, each compound has its own individual set of molecular parameters, and thus, all of the segments constituting the molecule are of the same size and energy. These represent "averaged means" able to represent the basic physical features of the compounds but that do not explicitly account for the heterogeneity of the molecules or the different functional groups present in their chemical structures.

To improve the predictive, or at least extrapolative, ability of association models, several authors have shown that simple empirical relationships between the pure-component parameters and M_w can be drawn for homologous series, allowing for extrapolation of parameters to compounds of different chain lengths. However, as the fluids involved become more complex, the performance of the extrapolated parameters deteriorates, especially for increased chain lengths if the underlying molecular model of the smaller oligomers is too simplistic or the parametrization was done solely around the lower molecular weight members.[46,126] Another approach

consists in the use of "pseudo group contribution methods", in which the values of the nonassociating parameters of a given species are obtained from mixing rules that combine values specifically obtained for each group constituting the molecule.[127−129]

Aiming at the development of more physically realistic models of enhanced predictability, less dependent on experimental data, heteronuclear approaches coupled to group-contribution methods have been used in the framework of SAFT-type EoSs.[37,38] As illustrated in Figure 3, this allows the study of chainlike molecules built from segments of different size and/or energy that can thus be related to distinct functional groups constituting the molecules. The advantages of these approaches is that once parameters have been determined for a number of functional groups (whose parametrization can be carried using a wider range of experimental data) and the unlike parameters defined, one can easily predict the thermodynamic behavior of a virtually unlimited number of compounds without further fitting. This has, however, been seldom used to model EO containing compounds in spite of the promising results reported, and despite this being a more physically sound approach to describe glymes.

Another widely used oversimplification has been to assume that the hydrogen bonding character of the EO groups does not need to be explicitly accounted for by the molecular models, but rather implicitly through the specific values of the pure-component parameters without the inclusion of additional association sites, avoiding the increasing computational cost when computing the association term of SAFT-type EoS. This becomes a particularly crude simplification when dealing with dialkyl glymes, where, as no hydroxyl end-groups are present, they have been frequently modeled as nonassociating species as if dealing with n-alkanes.[43,114,115] This may result in inaccurate description of the systems when the molecular models developed in this way are applied to the modeling of complex cross-associating mixtures.[114]

When association sites are added to represent the lone electron pairs on the inner oxygen atoms, there is no agreement between the different authors with respect to the most appropriate association scheme or number of association sites to be used with the choice pending to the one providing the best agreement with the experimental data when using that model.[122] Moreover, when additional sites are added to the molecules, they all share the same energy and volume parameters, regardless the functional group they are intended to mimic.[74] This, although decreasing the number of unknown molecular parameters a priori, represents a simplification of the molecular models whose influence has not been properly addressed so far.

Moreover, despite glycols and glycol ethers represent a very large group of compounds with several applications across different industrial fields, there is a huge gap in the literature for simultaneous investigations of these compounds regardless of their chain length (e.g., glycol oligomers and PEGs are usually investigated separately) or terminal end-groups (e.g., glycols and glycol ethers) since they are constituted by the same functional groups. Such studies could provide the missing link for the development of an integrated thermodynamic modeling approach that could address all these similar yet different compounds.

Furthermore, and considering that many glycol ethers are useful for industry due to their surfactant-like behavior, it is

important to highlight that understanding and modeling surfactant-like behavior is a nontrivial and cumbersome task. Although great progress has been made in different experimental aspects, the theoretical understanding of surfactant solutions is still poor, hindering the development of a complete thermodynamic framework that would allow the determination of characteristic properties such as surface tension, cloud point, aggregation numbers, CMC, and Kraft temperature. Nowadays, most of these properties are investigated using molecular dynamics (MD) simulations using semiempirical coarse-grained (CG) models whose optimal force field parameters are often found by a trial and error approach representing a huge computational effort without assuring an optimal solution. Therefore, the development of thermodynamic approaches based on analytical models such as EoSs could represent a significant improvement upon the parameters optimization span and speed. This is however, a poorly studied topic in the literature despite some promising results obtained in the determination of thermodynamic properties of surfactant systems using SAFT-type EoSs such as their phase behavior,[18,122] CMC,[120,121] or aggregation numbers.[123]

An attractive alternative would consist of merging both approaches. Theoretical models have undeniable advantages in terms of computational efficiency but cannot provide important structural information contrary to molecular simulations. Therefore, attempts to transfer the molecular parameters from EoSs to force fields used in MD simulations (top-down approaches) as reported by Jackson and co-workers[130−136] or vice versa (bottom-up approaches) should be systematically investigated, aiming at the development of a thermodynamic framework for studying surfactant-like behavior. Nonetheless, the "translation" of the SAFT association term into the simulations seems to be one of the biggest challenges yet to be addressed.

As a conclusion, further studies regarding different aspects of the thermodynamic modeling of compounds containing ethylene oxide groups such as the use of more complex methodologies (heteronuclear variants of SAFT, GC methods, more realistic association schemes), transferability assessments to different chain lengths and families of compounds (glycols to glymes and vice versa), and benchmarking with standard models such as SRK-HV are required in order to provide engineers with a unique answer on how to properly use association models to describe such compounds. Until then, the best approach will remain specific to a given system, application, or property, while the SAFT or CPA variant chosen is expected to play only a minor role.

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Notes
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