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Phase equilibria of aqueous solutions of formaldehyde and methanol: Improved approach using UNIQUAC coupled to chemical equilibria

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ABSTRACT

The study of the phase equilibria involving formaldehyde is still relevant because of its presence in new processes where biomass is the raw material. The coupling between physical phase equilibria and chemical reactions makes its thermodynamic description a challenging task. In this work, an improved approach using UNIQUAC coupled to chemical equilibria was developed and compared with experimental data from the literature. The first application was done for the phase equilibria of the formaldehyde–water system and distribution of oligomers in the liquid phase was computed. The second and the third applications respectively considered the phase equilibria of the formaldehyde–methanol system and the formaldehyde–water–methanol system.

1. Introduction

Formaldehyde has been used for long as intermediate chemical in several industrial processes (such as polymers production [1], adhesive synthesis [2], trioxane production [3], formaldehyde distillation [4,5]). Because of its acute toxicity (corrosivity, carcinogenicity, mutagenicity and reprotoxicity), its use is declining but studies about systems involving this compound are still relevant either because they are useful for depollution processes [6,7] or because emerging processes where lignocellulosic biomass is the raw material are likely to generate this compound. This is for instance the case for thermal processes like torrefaction [8,9] where formaldehyde was shown to be present in large amount in the gaseous effluent alongside other compounds including water and methanol. Because of its specific nature, modeling the behavior of formaldehyde is an important step for understanding and controlling of thermal processes involving lignocellulosic biomasses in general. Indeed, formaldehyde is also present in pyrolysis oils [10] and should be taken into account for depollution processes.

Formaldehyde is the smallest aldehyde molecule and is a gas at ambient conditions. It is highly soluble and reactive in water. Therefore formaldehyde is commonly handled in aqueous and/or methanolic solutions that stabilize it, the most common being known as formalin, an aqueous solution of formaldehyde and methanol containing between 37% and 41% of formaldehyde. Indeed, aqueous solutions of formaldehyde and methanol are not simple ternary systems because formaldehyde reacts with both methanol and water to form diverse polymers. Thus, formaldehyde is not stored or processed as a pure substance. Reactions with water generate methylene glycol, and poly(oxymethylene) glycols. Reactions with methanol form hemiformal and poly(oxymethylene) hemiformals.

This leads to a great complexity for the description of phase equilibria of this system and surprisingly, very few works are present in the literature. The most comprehensive studies originate from the group of Maurer at the University of Kaiserslautern (Kaiserslautern, Germany) and constitute the reference for this domain. Data from this group were used in this work [11–18]. The model established by this group was used as a basis for our improved approach that was assessed by comparison to experimental data and the original model.

2. Description of the reactive vapor–liquid equilibrium model

As mentioned above, when modeling the thermodynamic behavior of such systems, the main difficulty is to account for

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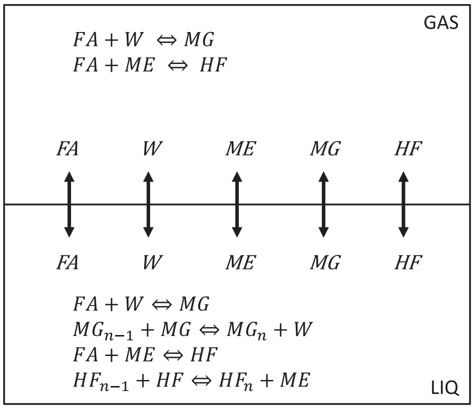

Fig. 1. Scheme of the vapor–liquid phase and chemical equilibria for aqueous solution of formaldehyde and methanol.

the coupling of chemical and physical equilibria of these reactive molecules. In this work, the physical and the chemical phenomena were implemented in a uncoupled way in the model so as to differentiate the effects of weak intermolecular interactions of the physical equilibria from the strong intermolecular interactions involved in the chemical reactions. For the vapor–liquid equilibrium a heterogeneous approach was adopted: the physical interactions between all species are taken into account through activity coefficients calculation in the liquid phase and through an equation of state for the gas phase. In this study, chemical reaction equilibrium constants are not considered as variables. The only variables to be estimated are the binary interaction parameters. Fig. 1 illustrates the outline of this model. Note that the system is described at equilibrium and no kinetic data are introduced in the modeling. Thus, the thermodynamic problem includes both:

- chemical equilibria of the methylene glycol, hemiformal, poly(oxymethylene) glycols, and poly(oxymethylene) hemiformals formation and
- physical phase equilibria of water, methanol, formaldehyde, methylene glycol and hemiformal.

This description of phase equilibrium in chemical reactive mixtures was formerly proposed by Maurer [11] and applied to aqueous solutions of formaldehyde and methanol. The UNIFAC Original model was chosen to represent the physical phase equilibrium. The advantage of the UNIFAC Original method lies in its predictive aspect but an important limitation is the influence of so-called proximity effects which are not accounted for. Indeed, for mixtures containing small molecules, the environment has a strong effect on the phase equilibrium. In this work, chemical description of the Maurer's approach was not modified but thermodynamic approach was improved using the UNIQUAC model. The main interest of the UNIQUAC model is the use of available experimental data for binaries to provide a more realistic description of the mixture behavior and for instance does not suffer from the limitations of UNIFAC Original, such as proximity effect. Moreover, it is able to account for size effects. Note that our approach is intended to be extended to the description of more complex mixtures containing other small polar molecules as encountered in gaseous effluents of wood torrefaction processes. A representative model of the system would allow proposing and designing a reliable separation process. In this case, the sole use of the UNIFAC Original model would give imperfect prediction.

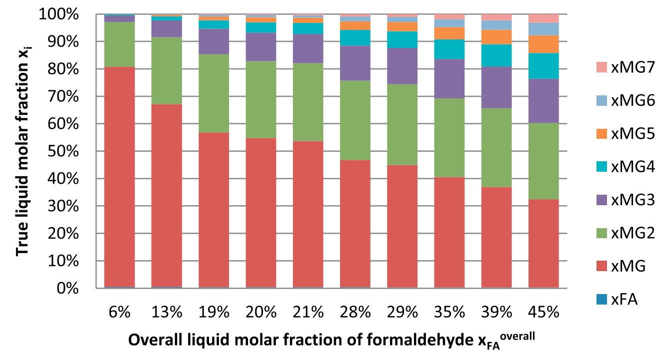

Fig. 2. Isothermal phase equilibrium for water–formaldehyde system at 353 K [17]: species distribution vs overall molar fraction of formaldehyde in the liquid phase.

2.1. Chemical reactions in aqueous and methanol formaldehyde solutions

Chemical equilibria are included in the thermodynamic description and chemical equilibrium is assumed. Formaldehyde is a very reactive component. In this model, the prominent reactions were assumed to be:

- formation of methylene glycol (MG): $CH_2O + H_2O \rightleftharpoons HO(CH_2O)H$;
- formation of poly(oxymethylene) glycols (MG_n): $HO(CH_2O)_{n-1}H + HO(CH_2O)H \rightleftharpoons HO(CH_2O)_nH + H_2O$;
- formation of hemiformal (HF): $CH_2O + CH_3OH \rightleftharpoons CH_3O(CH_2O)H$;
- formation of poly(oxymethylene) hemiformals (HF_n): $CH_3O(CH_2O)_{n-1}H + CH_3O(CH_2O)H \rightleftharpoons CH_3O(CH_2O)_nH + CH_3OH$.

The more concentrated the formaldehyde solution, the higher the degree of polymerization (see Fig. 2). Maurer's works considered polymers up to degree 4. Nevertheless, in this work, to obtain mass balance accuracy better than 5%, it was necessary to consider polymers up to degree 7.

Chemical reaction equilibrium constants are taken from the literature and follow a polynomial law: $\ln K = a_1 + a_2/T$. The coefficients are given in Table 1.

2.2. Description of the liquid phase

The major improvement proposed in this work is a better description of the thermodynamic behavior of the liquid phase. The physical interactions between all species are taken into account by an empirical approach based on local composition: the universal quasi-chemical model (UNIQUAC). UNIQUAC equations [20] are given by:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{1}$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{n} x_j l_j \tag{2}$$

$$\ln \gamma_i^R = q_i \left(1 - \ln \sum_{j=1}^{n} \theta_j \tau_{ji} - \sum_{j=1}^{n} \frac{\theta_i \tau_{ij}}{\sum_{k=1}^{n} \theta_k \tau_{kj}} \right) \tag{3}$$

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^{n} x_i r_i}; \quad \theta_i = \frac{x_i q_i}{\sum_{i=1}^{n} x_i q_i} \tag{4}$$

$$\tau_{ij} = \tau_{ij}^0 + \tau_{ij}^T (T - T_{\text{ref}}); \quad \tau_{ji} = \tau_{ji}^0 + \tau_{ji}^T (T - T_{\text{ref}}) \tag{5}$$

UNIQUAC is an empirical model that requires experimental data to identify binary interaction parameters. Therefore, it is not totally predictive as the UNIFAC model. This model has proved