

Co-Adsorption Equilibria from Liquid Mixtures containing Formaldehyde, Methanol and Water on Molecular Sieves 3A

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In this work, the co-adsorption equilibria from binary and ternary liquid mixtures of the system (water + methanol + formaldehyde) on molecular sieves 3A are studied in form of isotherms at two different temperatures. A model, which simultaneously considers the physical adsorption equilibrium and the chemical equilibrium in the bulk phase, is regressed to experimental adsorption data of the three binary subsystems. This model predicts the adsorption from ternary mixtures with good accuracy. Thus, it provides a solid basis for the design of adsorption processes with a wide range of applications, e.g. in the production of poly(oxymethylene) dimethyl ethers.

1. Introduction

Formaldehyde (FA, CH_2O) is an important intermediate for polymers, resins, and other chemicals. Recently, poly(oxymethylene) dimethyl ethers (OME), which are synthetic diesel fuels able to reduce the soot formation during the combustion, came into the scene as another important example of a formaldehyde-based product. Not only in the production process of formaldehyde, but also in subsequent processes the chemical system formaldehyde + methanol (ME, CH_3OH) + water (WA, H_2O) has to be dealt with. This system has a complex reactive nature and is not easy to separate using standard techniques like distillation. Especially the separation of water out of such mixtures remains challenging. Take for example the OME production process by Schmitz et al. (2017). Therein, water needs to be removed from mixtures containing formaldehyde, methanol and further components. Distillation is no option due to several azeotropes in the mixture.

Adsorption of water from the liquid phase is an interesting option for these mixtures. While there is some academic literature on adsorption of the system (FA + ME + WA) in the gas phase (Carter et al. 2011, Bellat et al. 2019), only a few contributions consider adsorption from the liquid phase (Novikova et al. 2019, Pahl et al. 2012, Schmitz et al. 2017). None of these studies include co-adsorption measurements.

For reliable process design of water removal by adsorption, more experimental data is needed. It has to be uncovered whether there is co-adsorption, i.e. whether and to what extent other species (besides water) adsorb as well. The aim of the present work is to provide exactly these measurements. Co-adsorption equilibrium experiments from the liquid system (FA + ME + WA) on molecular sieves 3A are done. A physico-chemical model is presented, which explicitly takes account of the chemical reactions occurring in the bulk phase. The model is fitted to binary systems and enables prediction in the ternary system.

This paper is structured as follows. In Chapter 2, some fundamentals of formaldehyde systems are presented. Chapters 3 and 4 describe the experiments and the model, respectively. The results are presented and discussed in Chapter 5 before we conclude.

2. Formaldehyde solutions

2.1 Chemistry of formaldehyde solutions

In aqueous solutions, formaldehyde forms poly(oxymethylene) glycols (MG_n , $\text{HO}(\text{CH}_2\text{O})_n\text{H}$) according to:





In a similar way, in presence of methanol, formaldehyde forms poly(oxymethylene) hemiformals (HF_n , $\text{HO}(\text{CH}_2\text{O})_n\text{CH}_3$):



All Reactions (1) – (4) have appreciable rates at all pH values and do not require any catalyst to occur. The chemical equilibrium of Reactions (1) – (4) is far on the product side, i.e. the amount of monomeric formaldehyde in aqueous and methanolic solutions is fairly small.

2.2 True and overall concentrations

In methanolic and/or aqueous formaldehyde solutions it is common to express the concentrations in two different ways: (a) true concentrations take account of all poly(oxymethylene) glycols and poly(oxymethylene) hemiformals; (b) overall concentrations refer to the concentrations that would be obtained when all species react back in Reactions (1) – (4) to formaldehyde, water and methanol. Overall concentrations, loadings, etc. are indicated with a $\sim$ above the respective variable. E.g. $\tilde{x}_{\text{FA}}$ represents the overall mass fraction of formaldehyde.

3. Experimental section

3.1 Adsorbent, chemicals and analysis

Adsorption based on the concept of size exclusion in microporous systems is used. Molecular sieves 3A, also known as zeolite 3A, are very efficient adsorbents and widely used for drying alcohols and other organic compounds like dimethyl carbonate. Zeolite 3A has a window aperture of approximately 3 Å. However, true size exclusion separations are the exception since the difference in critical diameters is mostly not sufficient for total exclusion of the larger molecules (Ruthven 2011). Therefore, the size parameters allow to expect co-adsorption of all three compounds in the system considered in the present work.

Molecular sieves 3A in form of spherical pellets with a diameter of 1.6–2.5 mm were purchased from Carl Roth. Paraformaldehyde (> 0.95 g/g) was acquired from Sigma-Aldrich. Methanol (> 0.999 g/g) was purchased from Merck. Ultra-pure water was obtained from an UP-System.

The overall mass fraction of formaldehyde was determined by the sodium sulphite titration (Walker 1964). The overall mass fraction of water was analysed using Karl Fischer titration. The overall mass fraction of methanol was obtained as the complement to 1 g/g.

3.2 Preparation of the solutions and pre-treatment of the molecular sieves

Aqueous formaldehyde solutions were prepared by dissolving paraformaldehyde in ultra-pure water at 70 °C under stirring for 2–3 days. Methanolic formaldehyde solutions were obtained analogously but the temperature was set at 60 °C. The molecular sieves were dried before each experiment for 24 hours at 298 °C and atmospheric pressure.

3.3 Measurement of the adsorption equilibrium

The density-bottle method developed by Yu et al. (2005) was applied in this work to determine the overall adsorbed amount $\tilde{q}_i$ of each component i . First, a 50 mL glass measuring flask was weighed. Next, approximately 15 g of pre-treated molecular sieves were placed into the flask and weighed to calculate the mass of adsorbent. The liquid solution was then added to the flask, so that the level of the liquid was above the ring mark on the flask. The flask was weighed anew to determine the initial mass of liquid. The solid-liquid mixtures were allowed to equilibrate for at least 72 hours, as they were gently shaken. Previous experiments showed that this time was enough for the mixtures to reach the equilibrium. During adsorption, the liquid level decreased but remained above the ring mark. Then, the shaker was turned off and the flask was weighed to check that the evaporative loss was insignificant (in our experiments it was always lower than 1%). A 2 mL syringe was used to remove liquid from the flask until the liquid level reached the ring mark and the flask was weighed again to determine the mass of removed liquid. All experiments were minimally duplicated (normally triplicated) to ensure the reproducibility of the results.

The basis of this gravimetric method is the measurement of the density change in the solid-liquid mixtures during the adsorption, assuming that the volume of the adsorbent is constant upon this process. The adsorbed amount $\tilde{q}_i$ of each component i is determined from the mass balance.

3.4 Experimental plan

24 experiments with the binary subsystems (FA + WA), (WA + ME) and (FA + ME) and 7 experiments with the ternary system (FA + ME + WA) were done. The equilibrium liquid phase concentrations in these experiments are shown in Figure 1. Attainable concentrations were limited by the solubility of formaldehyde in water and methanol.

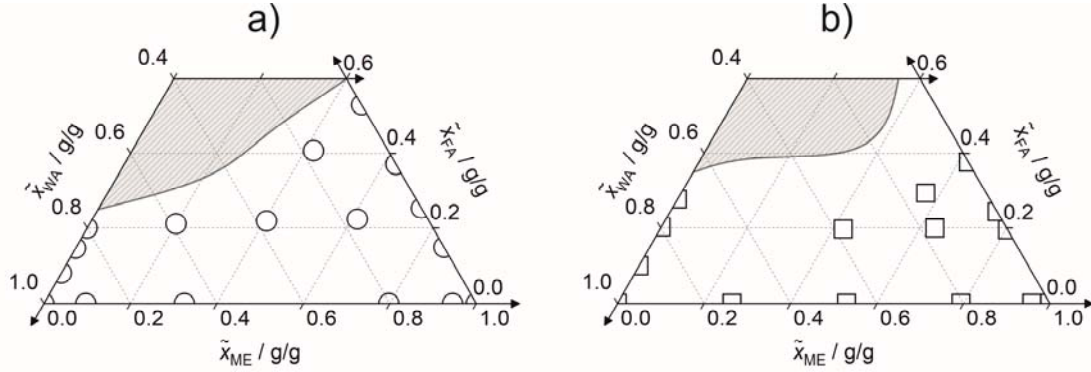


Figure 1: Experimental plan of this work at 22 °C (a) and 40 °C (b). Grey-shaded area: formaldehyde precipitation (qualitatively).

4. Modelling

4.1 Model description

Several multi-component models are available in the literature, including extensions of Langmuir, Freundlich and Sips isotherm models, cf. Rubiera Landa (2016) for an overview. In the present work, we have selected a multi-component Langmuir model. As described above along Reactions (1) – (4), only small amounts of formaldehyde are present in molecular form in the liquid phase. Most of the formaldehyde is chemically bound in molecules of larger size. This is expected to have major influence on the adsorption equilibrium, so it is advisable to use true concentrations instead of overall ones. To measure the concentration, i.e. driving force, the activity (Raoult's normalization) is used. The adsorption equilibrium is described by:

$$\tilde{q}_i / \text{g/g} = \frac{q_{m,i} \cdot K_i \cdot a_i}{1 + K_{FA} \cdot a_{FA} + K_{WA} \cdot a_{WA} + K_{ME} \cdot a_{ME}} \quad ; \quad i = \{\text{FA}, \text{WA}, \text{ME}\} \quad (5)$$

where a_i is the activity of the component i in the bulk liquid phase. $\tilde{q}_i$ is the overall adsorbent loading, i.e. the mass of adsorbed overall component i per mass of adsorbent. The correlation parameters $q_{m,i}$ and K_i are fitted to the experimental results. It is assumed that poly(oxyethylene) glycols and poly(oxyethylene) hemiformals are not adsorbed due to their large size.

The activity coefficients are calculated with a tailor-made UNIFAC parametrization adopted from Hahnenstein et al. (1995). The chemical equilibrium in the liquid bulk phase is explicitly considered using activity-based chemical equilibrium constants of the Reactions (1) – (4). The equilibrium constants are also adopted from Hahnenstein et al. (1995).

4.2 Implementation and parameter estimation

The model was implemented in the software MATLAB, where also the parameter estimation was done. Maximum experimental uncertainties were determined via error propagation for every experimental point individually. These maximum uncertainties depend mostly on the composition of the bulk phase and are quite different for the different experimental points. To account for these varying uncertainties, the parameters were estimations using weighted least squares with the objective function:

$$\min \sum_{k=1}^{N_{\text{exp}}} \sum_{i=1}^{N_C} \frac{1}{\sigma_{i,k}^2} \cdot (\tilde{q}_{i,k}^{\text{mod}} - \tilde{q}_{i,k}^{\text{exp}})^2 \quad (6)$$

Therein, i and k are counters for the number of components N_C and the number of experiments N_{exp} , respectively. Also, $\tilde{q}_{i,k}^{\text{mod}}$ are the modelled overall adsorbent loadings, $\tilde{q}_{i,k}^{\text{exp}}$ the experimental overall adsorbent loadings, and $\sigma_{i,k}$ the maximum uncertainties. For both temperatures, the parameters $q_{m,\text{ME}}$ and $q_{m,\text{WA}}$

were fixed to the values obtained for the pure components and the remaining four parameters were estimated by a simultaneous fit to all six binary isotherms.

5. Results and Discussion

5.1 Isotherm data

Experimental and modelled adsorption isotherms of the three binary systems at both temperatures are shown in Figure 2. The experimental uncertainties are shown by the error bars. The fit of the model is very good when put in relation with the experimental uncertainty. The adsorption capacities of water at 22 °C and 40 °C are 0.182 g/g and 0.181 g/g, respectively, which are in line with those reported by Teo et al. (1986) and Schmitz et al. (2017). The adsorption capacities of methanol at 22 °C and 40 °C are 0.121 and 0.135 g/g, respectively. The adsorption capacity for methanol had not been reported yet. It is not surprising that it is less (about 60 %) than the adsorption capacity for water because of the larger molecular size of methanol. Anyway, it is a novel fact since reference values for this quantity have not been found in the literature.

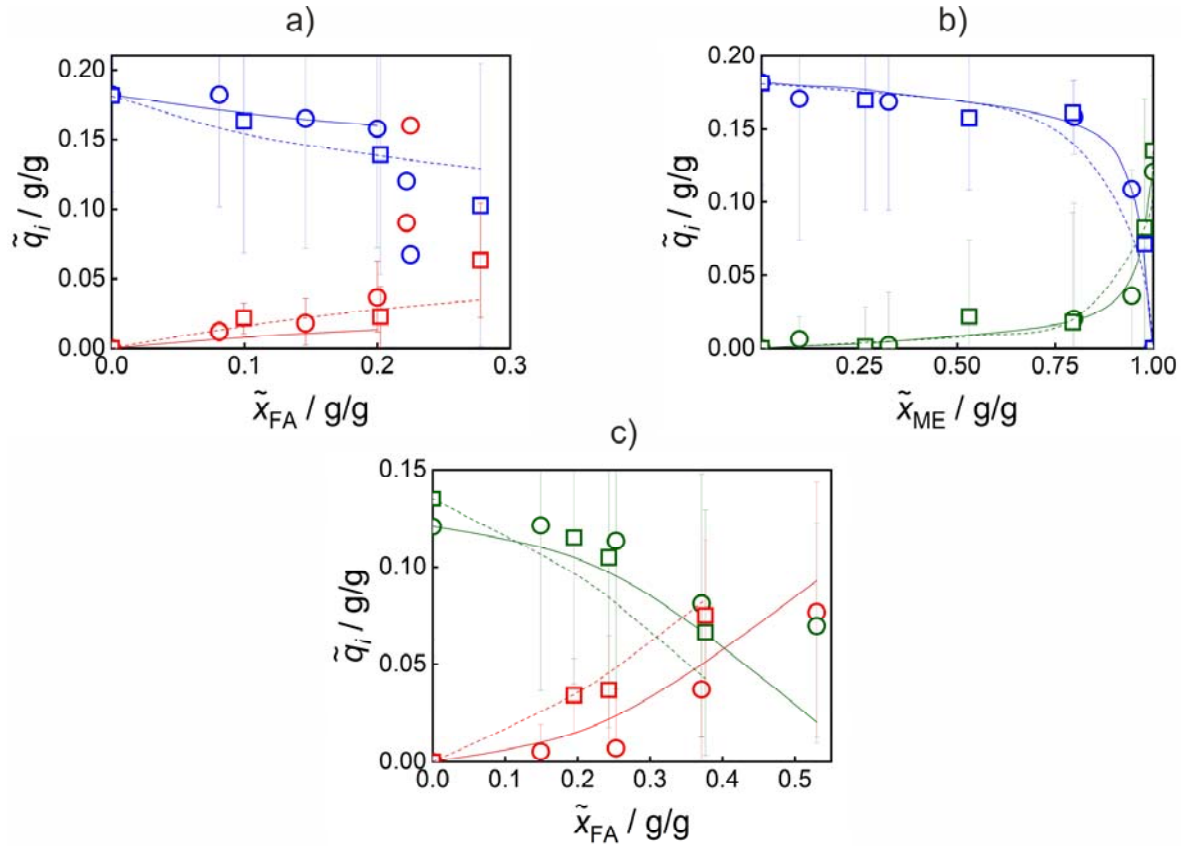


Figure 2: Co-adsorption isotherms of binary mixtures containing FA (red), ME (green) and WA (blue). a) ME + FA; b) ME + WA; c) WA + FA. Circles: measures at 22 °C. Squares: measures at 40 °C. Solid lines: model at 22 °C. Dashed lines: model at 40 °C.

For the binary mixtures containing formaldehyde and water at 22 °C, a very pronounced, almost vertical increase in the calculated values of $\tilde{q}_{FA}$ was observed for $\tilde{x}_{FA} \geq 0.22$ g/g. This value, $\tilde{x}_{FA} = 0.22$ g/g, concurs with the solubility of formaldehyde in water at 22 °C reported by Credali et al. (1965). No white precipitate was observed in the measuring flasks for $0.22 \text{ g/g} \leq \tilde{x}_{FA} \leq 0.30 \text{ g/g}$. However, the regeneration of the molecular sieves involved in these experiments was not effective through heating (298 °C, 1 bar) nor vacuum (180 °C, 100 mbar) since the measured adsorbed amounts by further experiments with these regenerated molecular sieves resulted negative. A similarly strong rise was observed for $\tilde{x}_{FA} \geq 0.28$ g/g for the same mixtures at 40 °C, which is also in line with the solubility of formaldehyde in water at 40 °C indicated by Credali et al. (1965). Therefore, it might be reasonable to assume that formaldehyde oligomers precipitate from the solution in the pores of the molecular sieves in these cases.

Figure 2c shows that the overall adsorbed masses of FA in methanolic solutions are clearly smaller than in aqueous solutions for a same overall mass fraction $\tilde{x}_{FA}$ of formaldehyde. This can be explained by the fact that the chemical equilibrium constant of Reaction (3) is significantly larger than the chemical equilibrium constant of Reaction (1) at the considered temperatures. This means that methanolic solutions contain much less monomeric formaldehyde than aqueous solutions at the same overall mass fraction of formaldehyde (Hahnenstein et al. 1995).

5.2 Influence of temperature

Figure 2b reveals that the influence of the temperature on the adsorption from binary mixtures containing water and methanol is not very substantial in the considered temperature range. Regarding the binary mixtures containing (FA + WA) and (FA + ME), the overall adsorbed mass of formaldehyde at 40 °C seems to be slightly larger than at 22 °C. This can be attributed to two competing effects. On the one hand, the overall adsorbed mass of formaldehyde decreases with increasing temperature because adsorption is an exothermic process. On the other hand, the amount of monomeric formaldehyde present in the liquid solution is larger at 40 °C than at 22 °C since temperature affects the chemical equilibrium of Reactions (1) – (4).

5.3 Ternary mixtures

Predicted and experimental adsorbed masses from ternary mixtures at 22 °C and 40 °C are compared in Figure 3. The agreement between predicted and measured adsorption values is good for all three compounds at both temperatures. The relative deviation of the predicted values of $\tilde{q}_{WA}$ with respect to the observed values are always smaller than 7 %. Overall-mass-fraction-based and true-mass-fraction-based models produced poorer agreement between predicted and experimental data. Despite the multicomponent Langmuir model does not explicitly consider interactions adsorbate-adsorbate nor adsorbate-adsorbent, does the introduction of the activity as modelling variable seem to properly describe the behavior of the studied system.

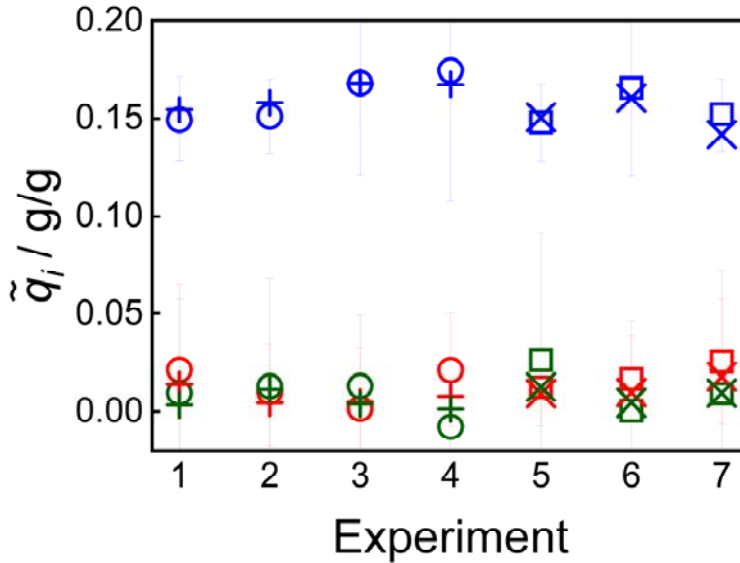


Figure 3: Predicted and measured adsorbed masses from ternary mixtures of FA (red), ME (green) and WA (blue). $\circ$: measurements at 22 °C, $\square$: measurements at 40 °C, $+$: predictions at 22 °C, $\times$: predictions at 40 °C.

6. Conclusions

Co-adsorption isotherms from liquid mixtures containing formaldehyde, methanol and water on zeolite 3A at two temperatures are reported. A physico-chemical model is regressed to the experimental results in the binary subsystems and used to predict co-adsorption from the ternary mixtures. The quality of the fit and prediction is within the experimental uncertainty. A change in the temperature affected both the adsorption and the chemical equilibrium in opposite ways, canceling out each other. The results of the present work serve as basis for the design of adsorption processes to separate water from (methanolic) formaldehyde mixtures.

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