



Coupled phase-reaction equilibrium for dihydromyrcene hydration system



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ABSTRACT

The solvent usually forms a large part of the heterogeneous hydration mixture in the biphasic hydration of liquid olefins, and solvent selection greatly affects the hydration conversion. In this work, the hydration of dihydromyrcene (DHM) in two different solvents, i.e., acetone and 1,4-dioxane, was investigated experimentally and mathematically. A theoretical model coupling liquid–liquid phase equilibrium and reaction equilibrium is proposed for evaluating the effects of the solvent on the heterogeneous hydration of DHM. Experiments were performed to obtain unreported parameters for the phase equilibrium and reaction equilibrium and the conversion of DHM in biphasic hydration was then predicted by the coupled model. The effects of the mass feed ratios on the total conversion X of DHM are discussed and varying conversions were observed when different solvents were employed. DHM was more soluble in the acetone system than in 1,4-dioxane, and the conversion of the hydration reaction was higher. This predictive evaluation process based on the overall equilibrium could provide a practical strategy for selecting the optimal solvent for the heterogeneous hydration of DHM and other liquid olefins.

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1. Introduction

The reversible hydration of liquid olefins with water is a typical liquid-liquid heterogeneous reaction and yields many valuable alcohol products and intermediates, such as cyclohexanol and terpineol. However, the interphase mass transfer problems in this biphasic system and the extremely slow reaction rates, both caused by poor miscibility between olefins and water [1,2], seriously hinder industrial applications of these reactions.

The use of solvents can increase miscibility of the reactants and homogenize the reaction mixture, thereby accelerate hydration and shorten the reaction time. However, great amounts of solvents are required, as well as large treatment capacity, to obtain a homogeneous hydration mixture, which is commercially unfavorable [3–7]. Partly for this reason, many modern-day industrial hydration processes are still performed in two liquid phases and suffer from low reaction rates, and the solvents in these processes can still account for up to 60% of the reaction mixture [8–12].

However, biphasic reactions can also offer advantages. Similar to the olefins themselves, their hydration products, i.e., the

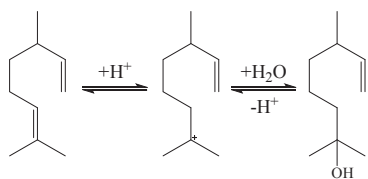
corresponding alcohols from liquid olefins, are usually immiscible with water [1,2,13–15]. During a biphasic reaction, these alcohols are synthesized in the aqueous phase and extracted into the organic phase. The continuous removal of products promotes forward hydration, which may increase the conversion by biphasic hydration. Evaluation of the advantages and disadvantages of monophasic and biphasic hydration can help identify appropriate methods for increasing the hydration of liquid olefins.

Most of studied on the hydrations of olefins were carried out in monophasic systems [16–22], while biphasic reactions were seldom involved. It is worth investigating the overall equilibrium of a heterogeneous hydration system in different solvents, which is a combination of the reaction equilibrium and phase equilibrium, and the understanding of the solvent effects on the overall equilibrium could provide a screening method for solvent optimization for a specific heterogeneous hydration.

This work focused on the direct hydration of dihydromyrcene (DHM) as a representative biphasic hydration. In the reaction, one of the double bonds in DHM is hydrated and the produced dihydromyrcenol (DHMOL) is one of the most popular perfumes worldwide.

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This hydration reaction has mostly been investigated in the monophasic [23–25] and low-boiling acetone has been suggested as a potential solvent as its use would help to reduce energy consumption [26].

In this study, the overall hydration conversion of DHM in the equilibrated system, in which phase equilibrium between the aqueous and organic phases and reaction equilibrium in the aqueous phase are both reached, was investigated. The coupled equilibrium was evaluated using the NRTL model and the reaction equilibrium model. The predicted results in two different solvents, i.e., acetone and the most commonly used solvent 1,4-dioxane, were compared and the effects of the solvents on the solubility and activity coefficients were discussed. Experiments on the liquid-liquid equilibrium (LLE) of the water + acetone + DHM system and the reaction equilibrium of DHM hydration in acetone were performed to obtain previously unreported parameters of the NRTL model and reaction equilibrium.

2. Phase-reaction equilibrium model

The industrial hydration of DHM is performed in a multiphase system that consists of two liquid phases and a solid resin catalyst phase. Hydrophilic resin catalysts tend to swell in water or other polar solvents [27] and become covered with a thin water layer during the hydration. The reaction can then be considered to take place only in the aqueous phase, therefore only liquid phases in the reaction are counted in this work, i.e., “monophasic” or “homogeneous” indicates one liquid phase, and “biphasic” or “heterogeneous” indicates two liquid phases in this paper.

During the reaction, the DHM in the organic phase transfers into the aqueous phase, reacts with adsorbed water, and produces DHMOL; the DHMOL is continuously extracted by the organic phase from water (Fig. 1). The hydration reaction in water is therefore pushed forward until both phase equilibrium between the two liquid phases and reaction equilibrium in the aqueous phase, which is the phase-reaction equilibrium, are achieved.

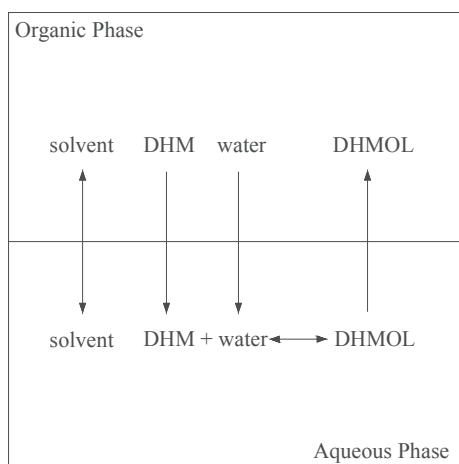


Fig. 1. Mass transfer and reaction in heterogeneous mixture.

When the phase-reaction equilibrium is reached, the following equations must be satisfied:

$$\text{Phase equilibrium } x_{\alpha,i}\gamma_{\alpha,i} = x_{\beta,i}\gamma_{\beta,i}, i = 1, 2, 3, 4 \quad (1)$$

$$\text{Reaction equilibrium } K_a = \frac{a_{\beta,4}}{a_{\beta,1} \cdot a_{\beta,3}} \Big|_{\text{eq}} \quad (2)$$

where x is the mole fraction; γ is the activity coefficient; K_a is the reaction equilibrium constant; subscript i ($= 1, 2, 3, 4$) represents the components water, solvent, DHM, and DHMOL, respectively; and subscripts α and β represent the organic phase and aqueous phase, respectively. The equilibrium concentrations of each component in the organic and aqueous phases can be predicted by solving the two equations.

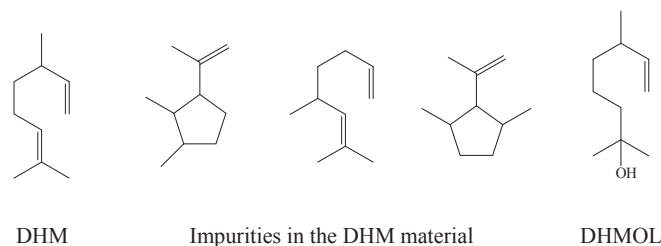
The LLE and reaction equilibrium data are needed to predict the phase-reaction equilibrium of the DHM hydration system. The LLE data at 343.2–358.2 K for the water + 1,4-dioxane + DHM + DHMOL system have been reported [7,14,28], as have the data for the reaction equilibrium of DHM hydration with 1,4-dioxane as the solvent [29]. The LLE data at 358–368 K for the water + acetone + DHMOL system have also been reported in our previous work [13].

In this study, LLE experiments for water + acetone + DHM and the hydration of DHM in acetone were performed to obtain the binary interaction parameters for the acetone + DHM system and the hydration equilibrium data for DHM hydration in acetone. These reported and experimental data can be used to calculate the phase-reaction equilibria of the DHM hydration in two different solvents, i.e., acetone and 1,4-dioxane.

3. Experimental

3.1. Materials

In this work, technical grade DHM (purity ≥ 89 wt%, CAS no. 2436-90-0, Huaian Wanbang Aromatic Chemicals Industry Co., Ltd.) was used in experimental measurements so as to more closely reproduce an actual industrial reaction. The main impurities in the DHM were isomers of DHM produced in the isomerization of α -pinane, the main method for producing DHM. The other chemicals listed in Table 1 were used without further purification. The hydration catalyst NKC-9 was purchased from the Catalyst Plant of Nankai University; the particle size was 0.40–1.25 mm. Distilled water was used in all experiments.



3.2. LLE experiments

The apparatus for the LLE measurements, which was described in detail in our previous work [13], consisted of a steel cell of capacity 50 mL equipped with a heating jacket and a temperature control system. Prior to each experimental run, a mixture of water, acetone, and DHM was added to the cell and the cell was sealed.

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