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Combined chemical and phase equilibrium for the hydration of ethylene to ethanol calculated by means of the Peng–Robinson–Stryjek–Vera equation of state and the Wong–Sandler mixing rules

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ABSTRACT

Due to the economics of the ethylene market and the subsidized production of fermentation-based ethanol in some countries, use of the ethylene hydration process to make ethanol has been steadily declining. The economics of this process might improve by combining the reaction and separation in a reactive distillation column, whose conceptual design requires a study of the combined chemical and phase equilibrium (CPE) of the reacting system. In this work, the Peng–Robinson–Stryjek–Vera equation of state was combined with the UNIQUAC activity coefficient model through the Wong–Sandler (WS) mixing rules in order to correlate the available experimental data for the vapor–liquid equilibria (VLE) of the ethylene–water, ethylene–ethanol, and ethanol–water binary systems at 200 °C. The interaction energies of the UNIQUAC model and the binary interaction coefficient of the WS mixing rules were used as the fitting parameters. From the optimum values of these parameters, both the VLE and the combined CPE of the ethylene–water–ethanol ternary system were predicted at 200 °C and various pressures. At this temperature, the catalytic activity of a H-pentasil zeolite has already been reported to exhibit a maximum for ethylene hydration, and also the experimentally measured two-phase region of the ternary system is sufficiently wide. By means of the reactive flash method, the chemical equilibrium compositions of the liquid and vapor phases were determined for several pressures, and the equilibrium conversion and the vapor fraction were calculated as functions of the ethylene to water feed mole ratio. It turns out that the vapor–liquid mixed-phase hydration of ethylene achieves equilibrium conversions much higher than those computed for a vapor-phase reaction that would hypothetically occur at the same conditions of pressure and feed mole ratio. It was found that the reactive phase diagram of the ternary system exhibits a critical point at 200 °C and 155 atm.

1. Introduction

1.1. Background

In the petrochemical industry, ethanol (C_2H_5OH) is produced from the catalytic hydration of ethylene (C_2H_4), according to the reaction:

$$C_2H_4 + H_2O \leftrightarrow C_2H_5OH$$

Ethanol produced from ethylene is known as synthetic (or petrochemical) ethanol. Synthetic ethanol is still used as an intermediate in the manufacture of other chemicals such as ethyl acrylate, ethyl acetate, ethylamines, diethyl ether, ethyl vinyl ether, ethyl tert-butyl ether, and glycol ethyl ethers [1]. Due to the unfavorable combination of high ethylene price and subsidized production of fermentation-based ethanol, use of the ethylene hydration process to produce ethanol has been steadily declining in some countries, e.g. the U.S.A., where only a single producer, Equistar Chemicals (a subsidiary of LyondellBasell Industries), remains in the field with its plant (with a capacity of 150 kt/year) at Tuscola, Illinois [2–5]. In contrast, synthetic ethanol is made at low cost in places where ethylene is cheap, e.g. Saudi Arabia, where 300 kt/year of crude ethanol are produced at Al-Jubail, by SADAF, a subsidiary of SABIC [1,3,6]. Europe's largest producers of synthetic ethanol are INEOS Enterprises with two plants at Grangemouth, Scotland (with a total capacity of 310 kt/year) [7,8], and Sasol Solvents Germany, with one plant at Herne, Germany, with a production capacity of 140 kt/year [9].

The vapor-phase direct hydration of ethylene, using phosphoric acid as catalyst, has been employed for the commercial production of synthetic ethanol since 1948 [10,11]. A calcined diatomaceous earth known as Celite used to be the preferred catalyst support until a porous silica xerogel was adopted [12]. The process of direct

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Table 1

List of works in which experimental measurements of high-pressure VLE have been reported for the ethylene–water, ethylene–ethanol, and ethanol–water binary systems, and the ethylene–water–ethanol ternary system.

System	Published work	Temperature range (°C)	Pressure range (atm)
Ethylene–water	Tsiklis et al. [33]	200–300	30–160
	Anthony and McKetta [34]	38–138	14–340
	Sanchez and Lentz [35]	150–300	99–691
Ethylene–ethanol	Tsiklis and Kofman [36]	150–220	10–127
Ethanol–water	Griswold et al. [37]	150–275	7–102
	Barr-David and Dodge [38]	150–350	5–187
Ethylene–water–ethanol	Tsiklis et al. [39]	200–300	30–160

hydration of ethylene consists of three sections: reaction, recovery and purification, and production of anhydrous ethanol. Brief descriptions of the process have been given in Refs. [1,13–17]. Detailed descriptions can be found in Refs. [11,18,19]. The ethylene to water mole ratio in the reactor feed is in the range of 0.3:1 to 4:1. Reaction temperatures are in the range of 210–325 °C. Reactor pressures are in the range of 30–100 atm. Use of high temperatures increases the reaction rate; however, since the reaction is exothermic [1,17–19], its equilibrium conversion decreases at higher temperatures, and the reaction is then limited by chemical equilibrium. In consequence, the temperature of the reactor should be set as a compromise between kinetics and thermodynamics. The gas–liquid mixed-phase hydration of ethylene, feeding gaseous ethylene and liquid water into a trickle-bed reactor [19], has been the subject of several patents [20–24] that use a mixture of titanium and tungsten oxides [20,22], the blue oxide of tungsten [21,23], or a dispersed alumina gel [24] as the catalyst. The water to ethylene mole ratio in the reactor feed is in the range of 16:1 to 54:1. Reaction temperatures are in the range of 240–310 °C. Reactor pressures are in the range of 100–350 atm. However, as far as is known [19], none of these patents led to any commercial applications.

Some technology enhancements for the vapor-phase direct hydration of ethylene have been proposed and described recently [25]. According to their proponents [25–27], these enhancements can improve the economics of the process in such an extent that they can make synthetic ethanol competitive with fermentation-based ethanol due to a simpler plant design, lower construction and operating costs, and a higher purity product [26]. The economics of the direct hydration of ethylene might improve further by applying the concept of process intensification [28,29]. In an intensified process, the reaction and the separation of the product (ethanol) and the reactants (ethylene and water) would occur in a single piece of equipment, a reactive distillation (RD) column. Indeed, ethylene hydration has been mentioned [30] as one of several potential applications of RD in the presence of a supercritical fluid (ethylene, in this case). A study of the combined chemical and phase equilibrium (CPE) of the reacting system is required for the conceptual design of an RD column [31,32].

1.2. *Prior work*

Table 1 provides a list of works [33–39] in which experimental measurements of VLE at high pressures have been reported for the ethylene–water, ethylene–ethanol, and ethanol–water binary systems, and the ethylene–water–ethanol ternary system. From the consideration of the typical temperature and pressure ranges for the ethylene hydration reaction (see Section 1.1) or the number of data points measured, the VLE data reported by Tsiklis et al. [33] for ethylene–water and Barr-David and Dodge [38] for ethanol–water were chosen for the present work.

No previous attempts have been made to correlate the VLE data reported by Tsiklis et al. for ethylene–water [33], ethylene–ethanol [36], and ethylene–water–ethanol [39]. Table 2 provides a list of works [40–51] in which equations of state (EoS) combined with excess Gibbs energy (G^E) models, through particular sets of mixing rules, have already been used to correlate (or predict) the VLE data reported by Barr-David and Dodge [38] for ethanol–water.

Table 3 provides a list of works [52–58] in which chemical equilibrium calculations for the vapor-phase direct hydration of ethylene have been reported. The temperature-dependency for the chemical equilibrium constant used in all these works was based on values of the standard properties of formation that turn out to be inaccurate by comparison with those more recently determined [59,60]. Ideal-solution behavior for the vapor phase was assumed in Refs. [52–54].

Table 4 provides a list of works in which combined chemical and phase equilibrium (CPE) calculations for the vapor–liquid mixed-phase hydration of ethylene have been reported. These calculations were based on some simplifying assumptions. The solubility of ethylene in the liquid phase was neglected in all three works and use of the gamma-phi formulation was made in Refs. [54,62] without applying any pressure-correction for the liquid-phase activity coefficients of ethanol and water, which were estimated in Ref. [62] from the isobaric VLE data of Otsuki and Williams [63] and correlated (by means of the van Laar model) in Ref. [54] from the VLE

Table 2

List of works in which equations of state (EoS) have been combined with excess Gibbs energy (G^E) models to correlate (or predict) the high-pressure VLE data measured by Barr-David and Dodge [38] for the ethanol–water binary system.

Published work	EoS	G^E model	Mixing rules
Gupte et al. [40]	vdW	UNIFAC-Lingby	VD
Schwartzentruber and Renon [41]	MSRK	UNIFAC	NQCD
Michelsen [42]	SRK	Wilson	IVI
Dahl and Michelsen [43]	MCSRK	UNIQUAC	MHV2
Wong et al. [44]	PRSV	van Laar	WS
Fischer and Gmehling [45]	MCSRK	UNIFAC	HFG
Hernández-Garduza et al. [46]	PRCRP	van Laar	RPSF
Constantinescu et al. [47]	MCSRK	$\text{UNIQUAC}^{\text{res}}$	HVID
Smith et al. [48]	PR	van Laar	SVA
Voutsas et al. [49]	MTPR	UNIFAC-Lingby	UMR
Shimoyama et al. [50]	SKYSRK	COSMO-RS	MHV1
Lee and Lin [51]	PR	$\text{COSMO-SAC}^{\text{res}}$	WS

vdW: van der Waals; SRK: Soave–Redlich–Kwong; MSRK: Mathias-SRK; MCSRK: Mathias–Copeman-SRK; SKYSRK: Sandarushi–Kidnay–Yesavage-SRK; PR: Peng–Robinson; PRSV: PR-Stryjek–Vera; PRCRP: PR-Carrier–Rogalski–Peneloux; MTPR: Magoulas–Tassios-PR; $\text{UNIQUAC}^{\text{res}}$: universal quasichemical residual contribution; COSMO-RS: conductor-like screening model for real solvents; $\text{COSMO-SAC}^{\text{res}}$: COSMO-segment activity coefficient residual contribution; VD: volume-dependent; NQCD: non-quadratic composition-dependent; IVI: implicit volume-independent; MHV2: modified Huron–Vidal second order; WS: Wong–Sandler; HFG: Holderbaum–Fischer–Gmehling; RPSF: reference packing fraction and scaling factor; HVID: Huron–Vidal with infinite dilution coefficient, SVA: Smith–Van Ness–Abbott; UMR: universal mixing rule; MHV1: modified Huron–Vidal first order.