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Measurement of the thermodynamic properties for the reactive system ethylene glycol–acetic acid

Bastian Schmid, Michael Döker, Jürgen Gmehling *

Carl von Ossietzky Universität Oldenburg, Technische Chemie, D-26111 Oldenburg, Germany

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Abstract

Isothermal vapor–liquid equilibria for eight binary systems of the reactive system ethylene glycol–acetic acid have been measured using a static VLE-equipment. Furthermore, excess enthalpies were determined with the help of an isothermal flow-calorimeter. Additionally, vapor pressure and density measurements of the monoacetylated ethylene glycol were carried out.

Keywords: Vapor–liquid equilibria; Excess enthalpies; Pure component properties; Reactive system; Experimental data

1. Introduction

The esterification of ethylene glycol with acetic acid is a reversible and consecutive nucleophilic second order substitution reaction whose mechanism is well known (Fig. 1). It is an interesting example for a reaction capable to be used for reactive distillation.

Although the monoacetylated as well as the diacetylated ethylene glycol is considered as an organic solvent and non-polluting fuel-additive, only a very small amount of thermodynamic data is published. Information of some applications is available in literature [1,2].

Reliable pure component and mixture data of the components involved is a precondition for the design and optimization of reactive rectification processes and other applications of industrial interest.

This work is part of our studies concerning the description of the reaction kinetics of the heterogeneous catalyzed esterification of ethylene glycol with acetic acid. In order to describe the reaction kinetics by means of activities one has to know the activity coefficients. These coefficients can be calculated with the help of G^E-models, such as UNIQUAC [3], whose parameters are fitted to experimental data. Up till now sufficient thermodynamic properties are only available for the systems water–acetic acid and water–ethylene glycol. Therefore, the measurement of vapor–liquid equilibria and excess enthalpies of 8 of the 10 possible binary systems had to be carried out as well as the measurement of pure component properties like vapor pressure and density data for ethylene glycol monoacetate. The investigated binary systems are given in Table 1.

2. Experimental

2.1. Chemicals and purities

Ethylene glycol and acetic acid were purchased from Sigma–Aldrich, ethylene glycol diacetate from Acros Organics. Ethylene glycol monoacetate was synthesized and purified in our laboratory. In order to obtain ethylene glycol monoacetate with a sufficient purity, the reaction of ethylene glycol with acetic acid catalyzed with the acid ion-exchange resin Amberlyst 36 from Rohm and Haas was carried out in a 2 l flask. After neutralization ethylene glycol monoacetate was extracted from the reaction mixture first with diethyl ether, later with chloroform. The solvent was removed at reduced pressure with the help of a rotating evaporator.

After drying over molecular sieves, degassing and distilling as described by Fischer and Gmehling [4], final purities were determined by gas chromatography (HP 6890 with Chemstation REV A.06.01 [403], auto sampler COMBI-PAL from CTC Analytics and analytical column HP1701 from Hewlett Packard)

* Corresponding author. Tel.: +49 441 798 3831; fax: +49 441 798 3330.
E-mail address: gmehling@tech.chem.uni-oldenburg.de (J. Gmehling).
URL: http://www.uni-oldenburg.de/tchemie (J. Gmehling).

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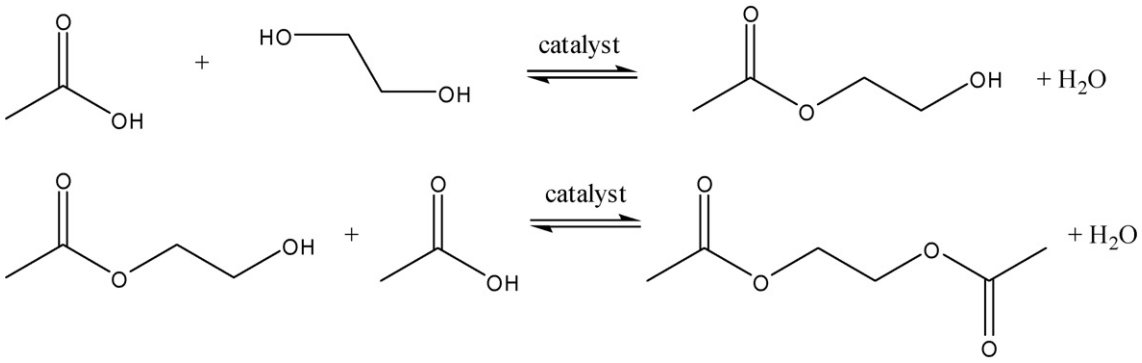

Fig. 1. Esterification of ethylene glycol with acetic acid.

using a thermal conductivity detector to >99.9%, ethylene glycol monoacetate to 99%. The water content was measured by Karl–Fischer titration [5]. De-ionized water was bi-distilled and degassed. The chemicals used including their purity and supplier are summarized in Table 2.

2.2. Pure component properties

2.2.1. Vapor pressure of ethylene glycol monoacetate

Vapor pressure measurement of ethylene glycol monoacetate has been carried out by means of a computer-aided ebulliometer which has been described previously [6].

The ebulliometer consists of a glass cell which is placed in a thermostat oil bath for heating. Thermal insulation is realized by a vacuum jacket. At the top of the cell the vapor space is connected via a reflux condenser to the computer-driven pressure regulating valves. Pressure regulation is realized by a D/A-converter. The pressure sensor and temperature sensor (Pt100, located in a tube filled with silicon oil in the cell and dipped into the sample) are connected to the serial ports of the computer. Measurement is completely handled by the controlling software which was developed in our research group. From 35 to 1013.15 mbar the accuracy is 0.05 mbar. The temperature can be measured with an uncertainty of 0.01 K from 280 to 620 K. The experimental data is given in Table 3 and Fig. 2.

2.2.2. Density of ethylene glycol monoacetate

A densitometer DMA 4500 from Anton Paar was used for the measurements of the densities of ethylene glycol monoacetate. The densities are determined at constant temperature from the vibration speeds of a glass U-tube filled with the reference fluids of well-known density and the compound considered. Care has to be taken that the sample is filled in the U-tube free of air bubbles. After the sample has reached the measurement temperature, a vibration is induced on one end of the U-tube and measured at the other end. Sensors are controlling and acquiring the data. The measurements have been carried out in 5 K steps from 283.16 to 343.14 K with an accuracy of ±0.01 K. The densities which are given in Table 4 and Fig. 3 were measured three

Table 1
Binary systems investigated in this work

First component	Abbreviation	Second component	Abbreviation
Water	H_2O	Ethylene glycol monoacetate	
		Ethylene glycol diacetate	EGDA
Ethylene glycol	EG	Ethylene glycol monoacetate	
		Ethylene glycol diacetate	
Acetic acid	HOAc	Ethylene glycol monoacetate	
		Ethylene glycol diacetate	
		Ethylene glycol	
Ethylene glycol monoacetate	EGMA	Ethylene glycol diacetate	

Table 2
Supplier and purity of the chemicals

Compound	Supplier	Purity [%]	Water content [ppm]
Acetic acid	Sigma–Aldrich	>99.9	9.4
Ethylene glycol monoacetate		99	96.8
Ethylene glycol diacetate	Acros Organics	>99.9	8.3
Ethylene glycol	Sigma–Aldrich	>99.9	46.7

Table 3
Vapor pressure data for ethylene glycol monoacetate

ϑ [°C]	P_i^S exp [kPa]	P_i^S calc [kPa]	ΔP	Deviation [%]
90	2.22	2.19	0.03	−1.37
101.27	3.79	3.79	0.00	0.00
130.51	13.81	13.64	0.17	−1.25
144.5	23.64	23.64	0.00	0.00
154.26	33.46	33.95	−0.49	1.44
161.75	43.30	44.33	−1.03	2.32
167.42	53.13	53.93	−0.80	1.48
171.1	62.95	61.08	1.87	−3.06
175.63	72.79	71	1.79	−2.52

Antoine parameters

A	8.25789
B	2874.45
C	273.038