PRODIAS
Processing Diluted Aqueous Systems

SPIRE PROJECT

Solid-liquid equilibrium in the system 2-Keto-L-gulonic acid + sodium hydroxide + water

Fabian Jirasek, Nadia Galeotti, Jakob Burger, Hans Hasse

Laboratory of Engineering Thermodynamics (LTD), University of Kaiserslautern, Germany

Introduction

2-Keto-L-gulonic acid (HKGA) is a key intermediate of the L-Ascorbic acid (Vitamin C) production process. The HKGA production process is one of the exemplary processes within the EU Horizon 2020 research project PRODIAS (Processing Diluted Aqueous Systems). After the fermentation HKGA is present within a highly diluted aqueous solution that also contains a large variety of process- and product-related impurities, including sodium salts. Crystallization offers a possibility to recover and simultaneously purify biotechnologically produced HKGA.

Regarding the crystallization of HKGA the knowledge of the solubilities of HKGA and its sodium salt NaKGA in water are of crucial importance. Within PRODIAS, physico-chemical properties relevant for the purification process of HKGA are experimentally measured and modeled. This work presents the experimental elucidation of the solid-liquid equilibrium in the system HKGA + NaKGA + water between 2 and 39.6 °C as well as the development of a thermodynamic model to describe the solid-liquid equilibrium.

Solid-liquid experiments

Procedure:

- Preparation of synthetic solid-liquid samples by mixing HKGA, NaOH and water
- Isothermal equilibration at temperatures ranging from 2.0 °C to 39.6 °C

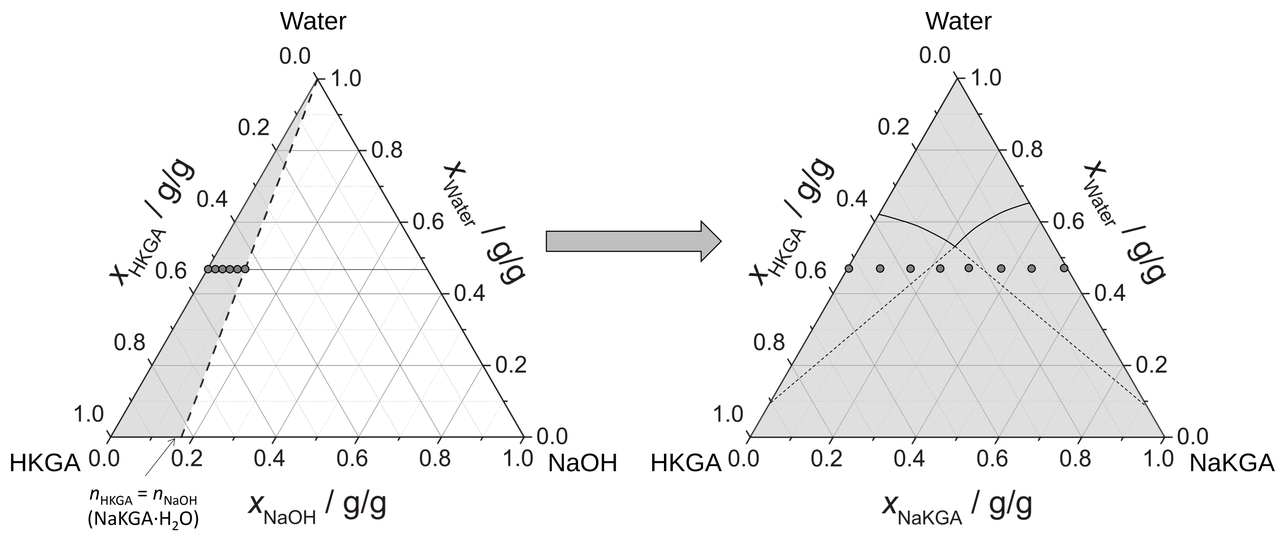


Fig. 1: Left: Phase diagram of the ternary system HKGA + NaOH + water. The dashed line marks the binary system NaKGA + water. The synthetic samples (circles) are located in the gray area. Right: Enlarged depiction of the gray area. The continuous line represents the solubility line in an eutectic system. The dashed lines mark the boundaries of the two-phase and three phase regions.

Analysis:

- Analysis of clear supernatant and wet solid residue
- Determination of concentrations of Na^+ and KGA^- ions by ionic chromatography

→ Determination of solubility and composition of the crystal phase

Binary systems HKGA + water and NaKGA + water

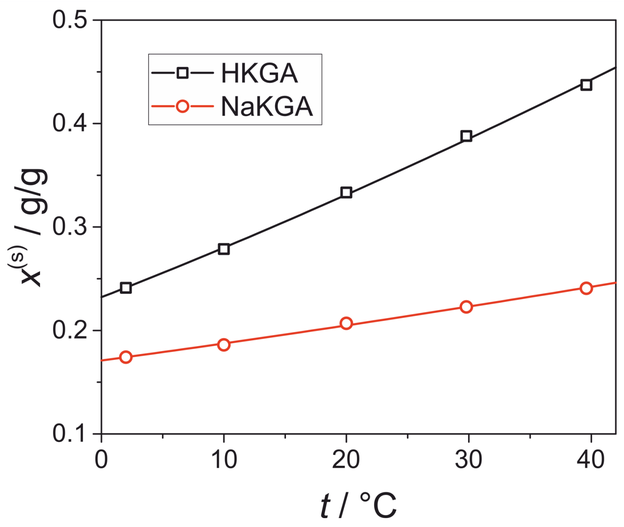


Fig. 3: Solubilities of HKGA and NaKGA (anhydrous mass) in water as a function of the temperature (symbols: experiments, lines: model).

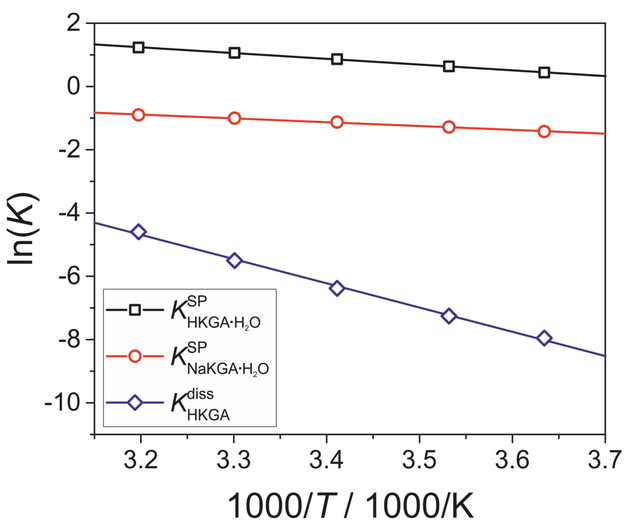


Fig. 4: Van't Hoff plot of the solubility products of HKGA·H_2O $\left(K^{SP}_{HKGA·H_2O}\right)$ and NaKGA·H_2O $\left(K^{SP}_{NaKGA·H_2O}\right)$ and the dissociation constant of HKGA $\left(K^{diss}_{HKGA}\right)$ (symbols: experiments, lines: model)

Van't Hoff equation and plot:

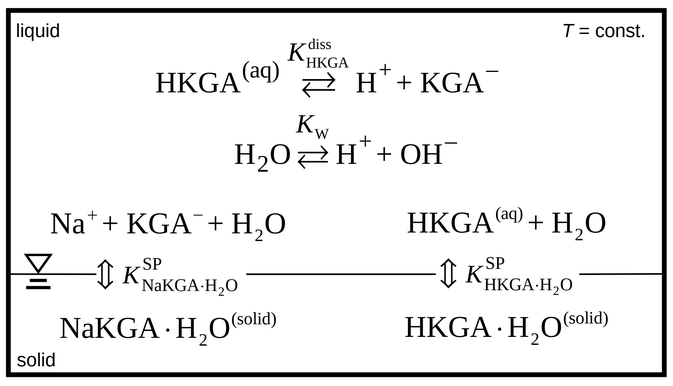
$$\ln K(T) = -\frac{\Delta\bar{h}^{o}}{R}\cdot\frac{1}{T}+\frac{\Delta\bar{s}^{o}}{R}$$

[o] Ideally diluted solution at $p = 1$ bar
Here: $\Delta\bar{h}^{o}, \Delta\bar{s}^{o} \neq f(T)$

Equilibrium constant	$\Delta\bar{h}^{o}$ / kJ/mol	$\Delta\bar{s}^{o}$ / J/(mol·K)
$K^{SP}_{HKGA·H_2O}$	15.1	58.7
$K^{SP}_{NaKGA·H_2O}$	10.0	24.7
K^{diss}_{HKGA}	63.7	164.9

Solid-liquid model

The species in the ternary solid-liquid system HKGA + NaKGA + water are described by four equilibrium processes (chemical reactions and phase transitions) (see Fig. 2).



$$K^{diss}_{HKGA} = \frac{m_{H^+}\cdot m_{KGA^-}}{m_{HKGA^{(aq)}}\cdot m_0}\cdot\frac{\gamma_{H^+}\cdot\gamma_{KGA^-}}{\gamma_{HKGA^{(aq)}}}$$

$$K_W = \frac{m_{H^+}}{m_0}\cdot\frac{m_{OH^-}}{m_0}\cdot\gamma_{H^+}\cdot\gamma_{OH^-}$$

$$K^{SP}_{NaKGA·H_2O} = \frac{m_{Na^+}}{m_0}\cdot\frac{m_{KGA^-}}{m_0}\cdot a_{H_2O}\cdot\gamma_{Na^+}\cdot\gamma_{KGA^-}$$

$$K^{SP}_{HKGA·H_2O} = \frac{m_{HKGA^{(aq)}}}{m_0}\cdot a_{H_2O}\cdot\gamma_{HKGA^{(aq)}}$$

Fig. 2: Schematic of the reactive solid-liquid equilibrium of the ternary system HKGA + NaKGA + water (left) and related equilibrium constants (right). Sodium salts are assumed to be completely dissociated in the liquid phase. HKGA and NaKGA are assumed to crystalize as monohydrate. m_j molality of species j in liquid phase, m_0 = 1 mol/kg, γ_j activity coefficient of species j in liquid phase, a_{H_2O} water activity.

Activity coefficient model for ionic species (extended Debye-Hückel model [1]):

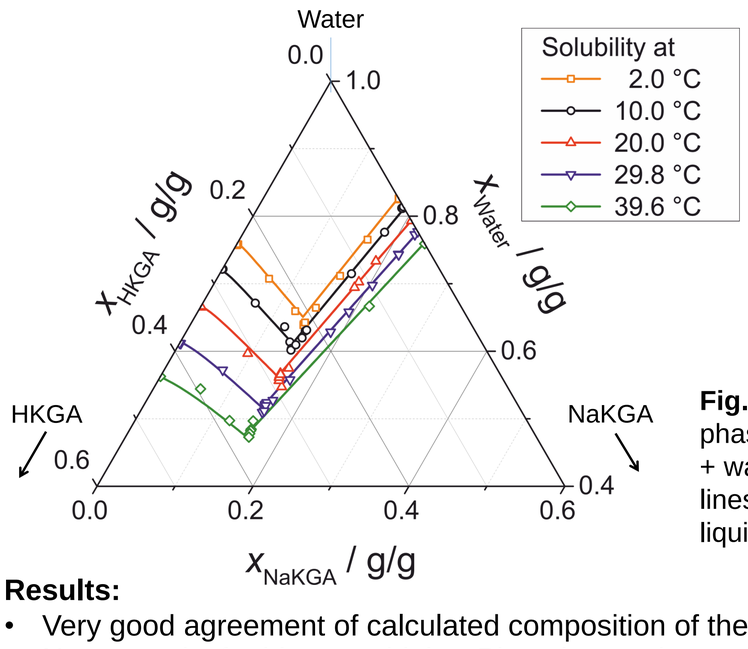
$$\ln\gamma_i = -A^{\Phi}\left(\frac{\sqrt{I}}{1+b\sqrt{I}}+\frac{2}{b}\ln\left(1+b\sqrt{I}\right)\right)$$

$$A^{\Phi} = \frac{1}{3}\left(\frac{2\pi N_0\rho_W}{1000}\right)^{\frac{1}{2}}\left(\frac{e^2}{\varepsilon_W kT}\right)^{\frac{3}{2}}$$

$$I = \frac{1}{2}\sum_i\frac{m_i}{m_0}\cdot z_i^2$$

A^{Φ}	Debye-Hückel coefficient
I	Ionic strength
b	Debye-Hückel parameter = 1.2 [2]
N_0	Avogadro's number
ρ_W	Density of water
e	Absolute elementary charge
ε_W	Static dielectric constant of water
k	Boltzmann's constant
T	Absolute temperature
z_i	Charge number of ion i

Ternary system HKGA + NaKGA + water



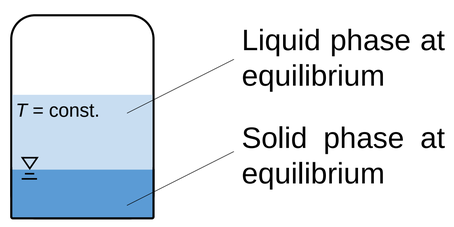


Fig. 5: Representative part of the solid-liquid phase diagram of the system HKGA + NaKGA + water. The symbols (experimental data) and lines (simulation) show the composition of the liquid phase at equilibrium.

Results:

- Very good agreement of calculated composition of the liquid phase with experimental results
- No necessity for binary or higher Pitzer interaction parameters
- The developed model offers a valuable tool for the HKGA crystallization process development

Summary and outlook

The solid-liquid equilibrium of the ternary system HKGA + NaKGA + water was experimentally determined at temperatures between 2.0 and 39.6 °C. A thermodynamic model was developed including an extended Debye-Hückel activity coefficient model. The predicted solubilities of HKGA and NaKGA in water as well as the crystallizing phase show very good agreement with experimental data. The model will be extended to multi-component systems in further steps to investigate e.g. the influence of other acids and salts on the solid-liquid equilibrium.

[1] K. S. Pitzer: The Journal of Physical Chemistry, Vol. 77, No. 2, 1973 [2] L. F. Silvester, K. S. Pitzer: Journal of Solution Chemistry, Vol. 7, No. 5, 1978

PRODIAS CONSORTIUM

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ABOUT THE PROJECT

- Start date: 1st January 2015
- Duration 48 Months, until 31st December 2018
- Budget: 14 million €
- Project web site: www.spire2030.eu/prodias/

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